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A TEXT-BOOK OF PHYSICAL CHEMISTRY

R. A. LEHFELDT

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A TEXT-BOOK

OF

PHYSICAL CHEMISTRY

BY

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PREFACE

THE establishment of the *Zeitschrift für Physikalische Chemie*, some twelve years ago, may be regarded as marking the rise of the science as an independent subject, and its recognition as such in Germany. About that time van 't Hoff published his extraordinarily fruitful ideas on osmotic pressure, and on the application of thermodynamics to chemistry; Ostwald was appointed to the chair at Leipzig, and the brilliant series of researches commenced, which have made that laboratory known throughout the world as the home of physical chemistry; and soon afterwards Arrhenius supplied, in the electrolytic dissociation theory, what was needed to complete the main outlines of the science. At the beginning of this decade physical chemistry was in the making: now it is so far set that a small text-book may be written with security and advantage; the subject is still growing very fast—as witness the 2,500 pages of the *Zeitschrift* every year—but the growth is in detail. It is time, too, to appeal for wider recognition in England, where, as yet, not a single professorship exists to mark the appearance of a new science that, on the Continent, has long been regarded as wide enough to require a man's whole energy.

The present book is intended to contain what a student—with limited time, and many subjects to learn

—may usefully read. It is by no means written to suit any examination, but still is written with the practical requirements of students in view—indeed, is based on the author's lectures. At the same time the author hopes that the style adopted will put the reader, as far as possible, in touch with the constant stream of experimental and theoretical research that makes physical chemistry at present such a fascinating subject to follow.

A good deal of mathematics is unavoidable; but it will be found that the mathematical sections can be left out without making the rest unintelligible. It may be pointed out that the earlier part of chapter iii, containing the general theory of thermodynamics, is not intended to be mathematically strict, but merely to indicate the course of reasoning followed by the strict proofs; for a thorough treatment of the subject, Planck's work should be consulted. In the latter part of that chapter the author has endeavoured to arrange the theorems on the application of thermodynamics to chemistry (and they gave him much trouble to understand) in the most intelligible form.

It is hardly necessary to express indebtedness to the classical writings of van 't Hoff, Ostwald, Nernst, and Planck: the short catalogue, following, of the leading books on theoretical chemistry will do so sufficiently, and in more useful form. It only remains for the author to add his gratitude to his friend Dr. F. G. Donnan, who read through the MS. and made valuable criticisms thereon.

LONDON,
July, 1899.

CONTENTS

PAGE

INTRODUCTION 1

Physical summary : Units 2

Fluid pressure 4

Elasticity 5

Laws of gases 6

Surface tension 8

Calorimetry 9

CHAPTER I

DETERMINATION OF MOLECULAR WEIGHT

§ 1. Molecular weight of gases 12

2. Molecular weight of vapours 16

3. Molecular weight in solutions : osmotic pressure . . 22

4. Vapour pressure of solutions 29

5. Boiling point of solutions 32

6. Freezing point of solutions 38

7. Practice of the freezing-point method 43

8. Dissociation of gases 47

9. Electrolytic dissociation 52

10. Laws of electrolytic conduction 55

11. Mechanism of electrolytic conduction 60

12. Measurement of conductivity 62

13. Molecular conductivity and electrolytic dissociation . . 66

14. Partial conductivity and velocity of the ions . . . 70

CHAPTER II

PHYSICAL CONSTANTS IN RELATION TO CHEMICAL CONSTITUTION

PAGE
§ 1. Density of fluids 76
2. Thermal expansion of fluids 79
3. Vapour pressure and critical point 81
4. Theoretical relations at the critical point: law of correspondence 83
5. Atomic volume 91
6. Refractive index 93
7. Dielectric constant 102
8. Viscosity 106
9. Surface tension: molecular aggregation of liquids . . 111
10. Constitutive properties: rotation of polarized light . . 116

CHAPTER III

THE PRINCIPLES OF THERMODYNAMICS

§ 1. The laws of thermodynamics 124
2. The first law 126
3. Application to a perfect gas 130
4. Reversibility 133
5. Entropy of a perfect gas 134
6. Entropy as the criterion of equilibrium in general . . 139
7. Deduction of the law of mass action 141
8. Thermodynamic equation between p, v, S, and T . . 145
9. Deduction of the influence of temperature on equilibrium . 148
10. Alternative deduction 151

CHAPTER IV

CHEMICAL DYNAMICS OF HOMOGENEOUS SYSTEMS

§ 1. Law of mass action 153
2. Chemical equilibrium: gases 157
3. Equilibrium in liquids 162
4. Avidity 167
5. Dissociation of water 171

PAGE
6. Hydrolysis 172
7. Influence of temperature on equilibrium 175
8. Velocity of reaction 178
    (*a*) Monomolecular reaction 179
    (*b*) Bimolecular reaction 181
    (*c*) Trimolecular reaction 184
9. Number of reacting molecules 185
10. Avidity measurements by means of velocity of reaction . 188
11. Velocity in reversible reactions 191
12. Temperature and velocity of reaction 193
13. Explosions 196
14. False equilibrium. 200
15. Influence of the medium on velocity of reaction . . . 203

CHAPTER V

Chemical Dynamics of Heterogeneous Systems

§ 1. The phase rule 204
2. Transition point 209
3. Delimitation of a system with one component : sulphur . 211
4. Delimitation of a system with two components . . . 214
5. Salt hydrates 215
6. Observation of transition points in condensed systems . 222
7. Simple and mutual solubility 225
8. General case of system of two components 229
9. Law of mass action in heterogeneous systems . . . 232
10. Henry's law. Law of partition 237
11. Relation between reaction constants and coefficients of solubility 241

CHAPTER VI

Application of Thermodynamics to Chemical Equilibrium

§ 1. Heat of reaction 244
2. Thermochemical methods 249
3. Classification of results 257
4. Application of the second law of thermodynamics . . 263
    (*a*) System of one component : heat of transition in condensed equilibrium 264
    (*b*) System of one component : heat of evaporation . . 264

PAGE
(*c*) System of more than one component: heat of transition in condensed equilibrium 266
(*d*) More than one componont: vapour pressure of dilute systems 266
(*e*) More than one component: osmotic pressure of dilute systems 269
(*f*) Homogeneous equilibrium 272

CHAPTER VII

ELECTRO-CHEMISTRY

§ 1. Origin of electromotive force 276
2. Measurement of electromotive force 278
3. Electromotive force at a single contact 280
4. Electromotive force of reversible electrodes . . . 284
5. Concentration cells 28
6. Polarization 292
7. Application of thermodynamics 296
8. Electromotive force and affinity 302

INDEX 306

The quantities occurring frequently in the course of the book are as far as possible expressed by the following symbols:—

C	Concentration.
D	Density of liquid.
E	Electromotive force.
F	Free energy.
G	$= \frac{K_P}{K_V}$ ratio of specific heats.
H	Quantity of electricity.
K	Reaction or dissociation constant.
M	Molecular weight (of dissolved substance)
P	Osmotic pressure.
Q	Quantity of heat.
R	Gas constant.
S	Entropy.
T	Absolute temperature.
U	Internal energy.
V	Dilution (c.c. per gram) of solution.
K_P	Specific heat of gas at constant pressure.
K_V	Specific heat of gas at constant volume.
Λ	Molecular conductivity.
d	Density of gas or vapour.
g	Acceleration of gravity.
kk'	Velocity of reaction.
l	Latent heat.
m	Molecular weight (of solvent or gas).
n	Number of ions formed from molecule.
p	Gas (or vapour) pressure.
q	Quantity of heat.
r	Valency.
uu'	Ionic velocities.
v	Molecular volume of gas or vapour.
x	Transference ratio of kation (Hittorf's number).
γ	Degree of dissociation, or degree of reaction.
ϵ	Quantity of electricity per gm. equivalent (96,540).
ι	Van 't Hoff's factor of dissociation.
κ	Specific conductivity.
λ	Molecular latent heat.
ν	Molecular coefficient in a chemical equation.

Some of the above symbols are, however, used *transiently* in other senses.

ABBREVIATIONS

In the references, the principal abbreviations used are:—

Ann. Chim. Phys. Annales de Chimie et de Physique. Paris : G. Masson. 8vo. Three volumes yearly in monthly numbers ; the present is the seventh series, begun in 1894. Each series usually lasts ten years.

Ber. Berichte der Deutschen Chemischen Gesellschaft. Berlin : Friedländer & Co. 8vo. One volume yearly.

Berl. Ber. Sitzungsberichte der Königl. Preussischen Akademie der Wissenschaften zu Berlin. Berlin : Georg Reimer. Lex 8vo. One volume yearly in parts. Called 'Monatsberichte' previous to 1882.

C. R. Comptes-rendus hebdomadaires des Séances de l'Académie des Sciences. Paris : Gauthier-Villars. 4to. Two volumes yearly in weekly parts ; volumes for 1899 are 128 and 129.

J. C. S. The Journal of the Chemical Society of London. London : Gurney & Jackson. 8vo. Two volumes yearly, numbered consecutively, one of transactions, one of abstracts.

Ostw. Zeitschrift für Physikalische Chemie. Hrsg. v. W. Ostwald und J. H. van 't Hoff. Leipzig : Engelmann. 8vo. Three volumes yearly in monthly parts. Volumes for 1899 are 28-30.

Phil. Mag. Philosophical Magazine and Journal of Science. London : Taylor & Francis. 8vo. Two volumes yearly in monthly parts. The present is the fifth series, volumes for 1899 being 47 and 48.

Wied. Annalen d. Physik und Chemie. Hrsg. von G. und E. Wiedemann. Leipzig : J. A. Barth. 8vo. Three volumes yearly in monthly parts. Volumes for 1899 are 67-69.

Of the numbers following the name of a journal, that in heavier type indicates the number of the volume : when a number in brackets precedes the volume number, it refers to the series.

SOME OF THE MOST IMPORTANT WORKS ON PHYSICAL CHEMISTRY ARE :—

J. H. van 't Hoff. Études de dynamique chimique (Amsterdam, 1884).
2nd edit., Studien zur chemischen Dynamik (Amsterdam, 1895).
Transl. of 2nd edit. by T. Ewan—Studies in Chemical Dynamics (London : Williams & Norgate, 1896).
Bildung und Spaltung von Doppelsalzen (Leipzig, 1897).
Vorlesungen über Theoretische und Physikalische Chemie (Braunschweig, 1898-9). Two volumes : third volume announced.
Transl. by R. A. Lehfeldt (London : Edw. Arnold, 1899).

W. Ostwald. Lehrbuch der Allgemeinen Chemie (Leipzig, 1st edit. 1885-87. Two vols.).
2nd edit., greatly enlarged, in course of publication. (This is by far the most complete work on the subject.)
Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen. (Leipzig, 1893.)
Transl. by J. Walker, 'Physico-chemical Measurements' (London : Macmillan, 1894).

M. le Blanc. Lehrbuch der Elektrochemie (Leipzig, 1896).

M. Planck. Vorlesungen über Thermodynamik (Leipzig, 1897).

W. Nernst. Theoretische Chemie (Stuttgart, 1893).
Transl. of 1st edit. by C. S. Palmer (London : Macmillan, 1895).
2nd edit. (Stuttgart, 1898).

LIST OF CHIEF PHYSICAL CONSTANTS

OCCURRING IN THIS BOOK.

		log.
Acceleration of gravity	980·61	2·991 4963
Atmospheric pressure (760 mm.) in dynes per sq. cm.	1,013.230	6·005 7080
Standard atmosphere adopted here (megadyne)	1,000,000	6·000 000
Gas constant in ergs	83,157,000	7·920 8988
,, in therms	1·9845	0·297 6495
Dynamical equivalent of heat (ergs)	42,000,000	7·623 2493
Absolute temperature of the freezing point	273	2·436 1626
One coulomb liberates 0·001118 gm. of Ag. and the atomic weight of Ag = 107·93, so that to liberate one gram equivalent requires, in coulombs	96,540	4·984 7073

INTRODUCTION

The science of physical chemistry, which is mainly a development of the last two decades, is not separated by any definite boundary from physics on the one side, or from chemistry on the other; but the accumulation of experimental material, and the growth of theory which allows of the experimental data being treated systematically, have made it convenient to regard physical chemistry as a distinct branch of the physical sciences. It consists chiefly in (i) measurement of the physical constants of chemically definite materials, and the relation between those constants and the chemical structure of the substances possessing them; (ii) the quantitative study of chemical reactions. These two divisions are frequently described as chemical statics and dynamics respectively. In this book the subject will be treated in the order just indicated, and—to explain the arrangement in somewhat more detail—physical constants may be measured either (*a*) to determine molecular weights (the subject of chap. i), or (*b*) for the more general problem of determining the structure of the molecule (chap. ii). Again, chemical reactions may conveniently be divided into those taking place in homogeneous systems (chap. iv) and those in heterogeneous systems (chap. v). To the whole is prefixed a short summary of the physical principles and conceptions involved; but one branch of physics, viz.

thermodynamics, requires special treatment on account of its importance and its difficulty. Thermodynamic reasoning is intimately bound up with the theories of physical chemistry; indeed the subject has come to be mainly built up on a basis of thermodynamic reasoning, and the application of thermodynamics is so certain, that not only may numerical observations be ranged in order by means of it, but one set of experiments may be made to determine the value of two quantities. Accordingly two whole chapters, Nos. iii and vi, have been devoted to an explanation of the principles of thermodynamics and their bearing on the problems of physical chemistry. Finally, the somewhat special phenomena of galvanic cells have been reserved for consideration in a chapter by themselves.

In the physical summary now to be given, no attempt at explanation will be made; the definitions and laws required for the subsequent treatment of physical chemistry will be stated simply for convenience of reference: for further explanation and illustration of their meaning the text-books of physics must be consulted. But it will probably be useful in reading the chapters following to have at hand a list of the leading physical constants, and of the algebraical relations between the various physical quantities.

Units.

According to the system generally adopted for the expression of physical quantities, three units, viz. those of length, time, and mass, are chosen arbitrarily, the remainder being derived from those. It has become customary to use the centimetre, the second, and the gram as the three fundamental units, and the set of units systematically derived from them constitutes what is known as the C. G. S. system. The principal quantities and their units are as follows:—

Length: unit, the *centimetre* (cm.).
Area: unit, the *square centimetre* (cm^2.).

Volume : unit, the *cubic centimetre* (cm^3. or c.c.).

Time : unit, the *second* (sec.).

Velocity, time-rate of change of position : unit, *cm. per sec.*

Acceleration, time-rate of change of velocity : unit, *cm. per sec. per sec.*

Mass : unit, the *gram* (gm.).

Density, mass per unit volume : unit, *gm. per c.c.*

Specific volume, volume per unit mass : unit, *c.c. per gram.*

Momentum, mass × velocity : unit, *gm. cm. per sec.*

Force, mass × acceleration (or time rate of change of momentum) : unit, *gm. cm. per sec. per sec.* called the *dyne.*

Energy (including work), force × distance : unit, *dyne-cm.* called the *erg.*

Power, time rate of change of energy (or rate of doing work) : unit, *erg per sec.*

Since the erg is an inconveniently small unit for practical purposes, use is frequently made of the

$$\textit{joule} = 10^7 \text{ ergs}$$

$$\text{and the } \textit{watt} = 10^7 \text{ ergs per second.}$$

Energy, the most important of these dynamical quantities, presents itself in the first place in the form of mechanical work. Work is done when motion is effected against the action of a force, and the amount of it is measured by the product of the force into the distance moved in the direction of the force. Energy may be defined as ability to do work, and is consequently a thing of the same kind as work, and to be measured in the same unit, the erg. There are many varieties of energy, but they may all be included under one or the other of two headings, viz. kinetic or potential. Kinetic energy is the energy possessed by a moving body in virtue of its motion ; it amounts to one-half the product of the mass of the body into the square of its velocity. Potential energy is the energy possessed by a body or system of bodies in virtue of their configuration (i. e. the mutual position of the parts of the body or system): such is gravitational energy, elastic energy, energy of electric charge, of chemical affinity, &c.

In addition to the above systematic units, in which nothing is assumed arbitrarily but the standards of mass, length, and time, a system is in use in which the unit acceleration is chosen arbitrarily, as equal to the acceleration of gravity on the earth's surface. This quantity is at any point the same for all bodies, and, moreover, varies little from place to place, having the average value of 981 cm. per sec. per sec. Accordingly the unit of force would then become the weight of 1 gram (i. e. the attraction of the earth on a gram mass, which would communicate to it an acceleration of 981 cm. per sec. per sec. if unopposed), and is equal to 981 dynes: it may be written 1 gm. wt. The unit of energy becomes the gram-centimetre or work done in overcoming a force of 1 gram weight through 1 cm. (e. g. in lifting 1 gm. through a height of 1 cm.), and is equal to 981 ergs. The above are called 'gravity' units, to distinguish them from the former 'absolute' or C. G. S. units. In this book the C. G. S. units will be regularly employed except in cases in which the gravity units occur inevitably, and then the latter will be converted into C. G. S. measure. The value of the acceleration of gravity, or g, varies from 978 at the equator to 983 at the pole: as a standard its value at sea-level in latitude 45° is adopted, and that is

$$g = 980{\cdot}61.$$

Fluid Pressure.

Fluids, i. e. liquids and gases, exert a pressure depending on their weight; this amounts at any point to the weight of a column of the fluid, of unit area, and of height equal to the vertical distance from the point considered to the top of the fluid: or symbolically

$$p = ghd \text{ (dynes per sq. cm.)},$$

where g is the acceleration of gravity, h the height, and d the density of the fluid. There may also be a pressure applied from without, as e. g. in the case of a liquid under ordinary conditions, which bears the weight of the atmosphere above it; but in any case the variation in pressure from point to point of the fluid is given by the above formula.

The pressure of the atmosphere is measured by that of the mercury column in a barometer. When the latter has its normal value of 76 cms. (corrected for temperature, &c., and reduced to the standard value of g) the pressure is

$$980{\cdot}61 \times 76 \times 13{\cdot}5956 = 1{,}013{,}230 \text{ dynes per sq. cm.}$$

This number is close to one million, and it is becoming customary to adopt one million dynes—or one *megadyne*—per sq. cm. as the standard atmospheric pressure. That unit will be employed in the following pages. It may be realized with sufficient accuracy by noting that it is very nearly equal to 75 cms. of mercury (exactly 75·0076 cms.).

Elasticity.

A *strain* is a change of size or shape.

A *stress* is that which produces a strain, and is measured by the amount of force exerted on unit area (pressure, tension, tangential force applied over an area).

Elasticity is the property of recovering from a strain when the stress is removed.

In all bodies the stress required to produce a *small* strain elastically is proportional to the strain produced (Hooke's law). The ratio

$$\frac{\text{stress}}{\text{strain}} = \text{coefficient of elasticity.}$$

Solids possess two independent kinds of elasticity—of volume and of shape. A strain in volume can be produced in an ordinary solid by a uniform (hydrostatic) pressure; it is measured by the ratio of the diminution of volume to the original volume. The stress (pressure) divided by the strain, so measured, gives the *coefficient of volume elasticity.*

A strain in shape only is a shear. It is measured by the ratio of the displacement of any point in the body to the distance of that point from the plane of the body which is not displaced. The shearing stress (tangential pressure) divided by the strain, so measured, gives the coefficient of elasticity of shape or *rigidity.*

Fluids are distinguished from solids by possessing no rigidity. Hence when a shear is set up in them, no elastic reaction occurs: if the stress be removed the fluid will not recover its former shape, and if the stress be maintained the amount of shear will go on increasing indefinitely. The shear then becomes a 'flow' of the material, to which there is a frictional resistance; the ratio

$$\frac{\text{shearing stress}}{\text{rate of shearing}}$$

is here a constant of the material, taking the place of the rigidity in a solid, and is called the *coefficient of viscosity.* The rate of shearing is to be measured by dividing the velocity of any point in the fluid by the distance of that point from the plane in the fluid which is not displaced; the stress is, as before, measured by the tangential force per unit area.

Laws of Gases.

Actual gases approximate to a condition known as that of a perfect gas, some of whose properties are as follows:—

When the temperature (T) remains constant, the pressure (p) of the gas is inversely proportional to its specific volume (v'), and therefore directly proportional to its density, or

$$p \propto \frac{1}{v'} (T \text{ const.}) \quad . \quad . \quad \text{(Boyle's law.)}$$

When the pressure remains constant, the specific volume is directly proportional to the absolute temperature (i. e. temperature measured from the absolute zero, about -273°C.), or

$v' \propto T\,(p \text{ const.})$ . . (Charles' or Gay-Lussac's law.)

When the volume remains constant, the pressure is directly proportional to the absolute temperature, or

$$p \propto T\,(v' \text{ const.}).$$

These three statements are summarized in the equation

$$pv' = R'T,$$

where R' is a constant: this is therefore called the 'characteristic equation' of the gas.

The gas constant is a quantity of great importance in physical chemistry, so that is desirable to evaluate it exactly. As defined above, it would have a different value for each gas; but, according to Avogadro's law, the specific volume of a gas is inversely proportional to its molecular weight, so that if in the equation the molecular volume (v) or volume occupied by one gram-molecule be used, the constant in the equation will be the same for all gases. We may therefore write

$$pv = RT,$$

in which the quantities refer to a gram-molecule of the gas. In order to determine R it would be sufficient to measure the volume of a perfect gas at any observed temperature and pressure. There is, however, no perfect gas. If oxygen be taken as the standard, it being commonly adopted as the basis of the system of atomic weights, we have, according to Rayleigh, Leduc, and others, the density 0·0014290 under a pressure of 1,013,230 dynes per sq. cm. and at the freezing point; but the gas being somewhat more compressible than a perfect gas, the theoretical density is 0·0014279 [1]. Hence, the molecular weight being taken as 32, we have

$$R = \frac{pv}{T} = \frac{1013230}{273} \times \frac{32}{0{\cdot}0014279} = 83{,}157{,}000 \text{ ergs.}$$

---

[1] D. Berthelot, *C. R.* **126.** 1030 (1898).

When the pressure exerted on a gas is high, it departs much in behaviour from a perfect gas; under some circumstances it may be liquefied, and the phenomena of the *critical point*, connecting gases with liquids, have to be considered. Various equations have been proposed to show more exactly the relation between the volume pressure and temperature of a fluid, of which the most important is that of van der Waals:

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT,$$

where a and b are constants. The equation to a perfect gas is a particular case of this with $a=0$ and $b=0$. The characteristic equation and its relation to the critical point will be reverted to in more detail in chap. ii.

Fluids possess one kind of elasticity only, that of volume. The coefficient of elasticity is obtained by dividing a small change of stress (pressure) by the corresponding small strain (or fractional change of volume). *For a gas obeying Boyle's law*, and *under the condition of constant temperature*, it may be shown that the coefficient of elasticity is numerically *equal to the pressure* of the gas.

[In the language of the calculus, the coefficient of elasticity $=\frac{vdp}{dv}$, which when $pv=$ const. becomes $=p$.]

For the molecular weight of a substance taken in grams the abbreviated expression *mol.* will be used.

Surface Tension.

In liquids there is a certain quantity of potential energy present associated with their surface, and proportional to its extent. This energy produces a tension across any line drawn in the surface of a magnitude (per unit length) numerically equal to that of the energy (per unit area), and shows itself in the well-known phenomena of capillarity. The surface energy or *surface tension* is most easily measured by the height to which the liquid rises in a capillary tube. For an ordinary liquid which wets glass, if D be the density of the liquid, d that of the vapour or gas in which the experiment is performed, h the height to which the liquid rises in a tube of radius r, and g the acceleration of gravity, then the surface tension is

$$\tau = \tfrac{1}{2} ghr(D-d) \text{ (dynes per cm.)}.$$

Calorimetry.

Heat is a form of energy, and may therefore be measured in terms of the erg. To measure a quantity of heat directly in ergs is not, however, always possible or convenient, so quantities of heat are usually expressed by a secondary unit which arises naturally in the mode of measurement, and the secondary unit is reduced to ergs by an independent experiment.

The secondary unit or *calorie* is usually defined as the quantity of heat required to raise 1 gm. of water through 1° C. Sometimes 100 or 1,000 times this amount is adopted, but such units will not be employed in this book.

The value of the calorie, however, varies slightly according to the degree of temperature through which the water is raised. The energy required—i.e. the value of the calorie—is shown for various temperatures by the following table:—

6°	4.203×10^7 ergs	1.0007 therms
10°	4.196	0.9990
15°	4.188	0.9972
20°	4.181	0.9955
25°	4.176	0.9943

These numbers are taken from the experiments of Rowland, as recalculated by Day[1], and expressed in terms of the constant-volume hydrogen thermometer.

It has been proposed to adopt as the standard calorie, or *therm*, the quantity 4.2×10^7 ergs. This is the value of the calorie at about 7·5°. The preceding table gives the means of reducing quantities of heat measured in a water calorimeter at other temperatures, to standard calories, or to ergs.

---

[1] *Physical Review*, 6. 193-222 (1898).

The *gas constant R* is approximately 2 calories.

The *specific heat* of a substance is the quantity of heat required to raise 1 gram of it through 1° C.

The *thermal capacity* of a body is the quantity of heat required to raise it through 1° C.

The *latent heat* of fusion (or of evaporation) of a substance is the heat required to melt (or volatilize) 1 gram of it. Sometimes the molecular latent heat is used instead. This is the heat required to melt (or volatilize) 1 gram-molecule of the substance.

The *heat of reaction* is the heat evolved when the quantities of reagents (in grams) expressed by the equation to the reaction suffer the chemical change in question.

The *heat of formation* of a substance is the heat that would be evolved in forming 1 gram-molecule of the substance from its elements.

It was found by Dulong and Petit that the specific heats of the solid elements are mostly in inverse proportion to their atomic weights. This may be expressed by saying that the *atomic heat* (specific heat × atomic weight) is constant.

The average value of this quantity is 6·4. The majority of the elements lie between 5·9 and 6·9, but a few have lower values. These are—

Aluminium	5·8	Beryllium (at 257°)	5·3
Gallium	5·5	Boron (at 600°)	5·5
Phosphorus	5·6	Carbon (at 1000°)	5·5
Sulphur	5·7	Silicon (at 232°)	5·7

The four latter elements have much lower atomic heats at atmospheric temperature. The atomic heat is, however, in any case, a very ill-defined quantity, varying much according to the temperature, crystalline form, and mechanical condition of the element.

The molecular heat of a solid compound is usually not far from the sum of the atomic heats of the constituents. The gaseous elements behave in solid compounds as if possessing the following atomic heats :—

Hydrogen	2·3	Chlorine	6·4
Oxygen	4·0	Fluorine	5·0
Nitrogen	6·4		

CHAPTER I

DETERMINATION OF MOLECULAR WEIGHT

§ 1. Molecular Weight of Gases.

If the problem of chemistry be regarded as that of relating the properties of bodies to their minute structure, i. e. to the configuration of the molecules of which they are supposed to be built up, it is clear that one of the first steps towards the solution of the problem, is to determine the mass of the molecules. With regard to the absolute masses, the information at present available is uncertain; but, fortunately, chemistry is not immediately concerned to know them: what is of far more consequence in the practice of chemistry is to know the relative masses of the various kinds of molecules, i. e. taking one kind—hydrogen or oxygen—as a standard, to measure the molecular mass, or as it is more commonly called, the molecular weight, of their bodies by comparison with it.

Until recently nothing was known as to the molecular weight of any substances except gases and vapours, but in the case of these a method of general application had been found. This is the method based on Avogadro's law. According to that law, all gases and vapours when under identical conditions of temperature and pressure contain equal numbers of molecules in the unit of volume; hence it is only necessary to measure the mass of unit volume, i. e. the density, to know the relative masses of the molecules.

The work of Regnault on gas densities was for many years the best of its kind, and although lately several experimentalists have made measurements which involve improvements of detail, a short account of his apparatus will sufficiently indicate the method to be followed. The method is essentially to weigh a globe (i) empty, (ii) full, of the gas in question at observed pressure and temperature, (iii) full of water, in order that from the difference between (i) and (iii) the volume of the bulb may be known: it is therefore the method of the specific gravity bottle, as applied to gases. The first and most obvious difficulty is that the gas in the globe weighs much less than the globe itself, so that small errors in determining the latter, due to air-displacement, moisture, electrification, &c., would produce a disproportionate effect on the weight of the contained gas. To minimize the error, Regnault weighed the working globe—a glass bulb of about 10 litres—against a bulb of the same size and weight as tare: both bulbs being similarly affected by temperature, pressure, and dampness of the air, there remained only the small difference of weight due to the gas contained, to compensate by weights from the box. The globe was closed by a metal tap—in all modern experiments a glass tap sealed on is preferred; through this it could be connected with the air-pump and the supply of gas. Regnault's air-pump was not capable of producing a complete vacuum, but modern mercury-pumps will easily evacuate a globe so completely that the residual gas—whose pressure may be less than one-hundredth of a millimeter—may be altogether neglected. With the aid of such a pump an experiment consists in evacuating the globe, heating it at the same time to drive off gas condensed on the glass surface, disconnecting from the pump, and placing on the balance; then, after sufficient time has elapsed for the bulb to acquire the temperature of the surroundings, and its surface to acquire a normal degree of dampness, in weighing against the comparison bulb ; afterwards the bulb is placed in ice, and a stream of the purified gas allowed to flow into it till the pressure is that of the atmosphere, or that indicated by a manometer attached to the filling apparatus. When the temperature and pressure are constant, the tap is closed again, the bulb carefully wiped dry, and reweighed. As considerable uncertainty is introduced by any handling of the glass surface, some experimenters have preferred to fill the bulb at the atmospheric temperature so as to avoid the necessity of wiping the glass, and reduce the weight to the standard temperature by the aid of a thermometer. A correction which is especially important in the case of hydrogen, overlooked by Regnault, and first pointed out of recent years, is due to the contraction of the bulb when the internal pressure is removed: this causes its displacement of air to be less when weighed empty than full, and it is necessary to add to the observed weight of each gas an amount equal to the weight of air displaced by the full bulb in excess of that displaced by the empty one.

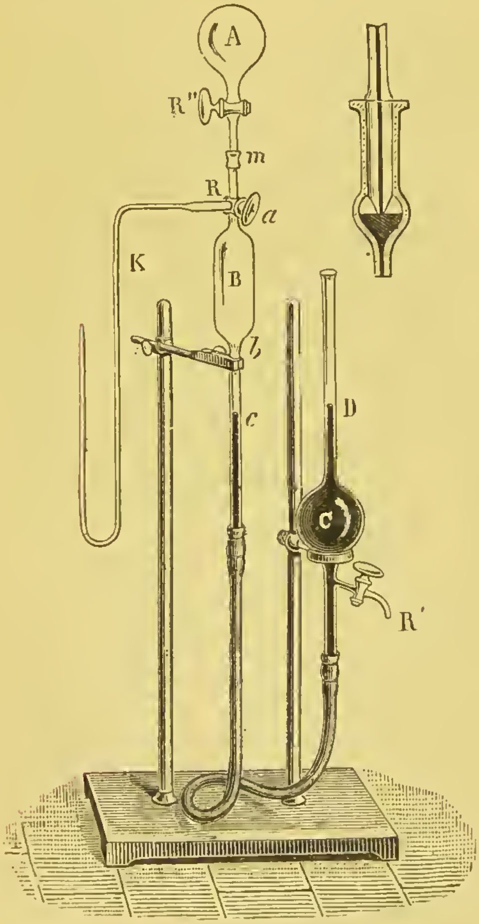

Fig. 1.

Very careful measurements of the density of hydrogen, oxygen, nitrogen, carbon dioxide, and air, have been made by J. P. Cooke, Lord Rayleigh, Leduc, E. W. Morley, and others, especially in the case of hydrogen and oxygen. For Avogadro's law, like the other gaseous laws, is only an approximation, and in order to determine the molecular weights of these gases two methods are available: either to find the combining proportions by weight directly, or to find the combining proportions by volume and reduce these numbers by the observed densities. Thus, according to Morley[1], 2·0027 volumes of hydrogen combine with one of oxygen to form water; but the density of oxygen is 15·9002 times that of hydrogen, so that the weight of oxygen which will combine with two grams of hydrogen is 15·9002 ÷ 2·0027 = 15·879; while Morley himself finds by gravimetric analysis the same number for the atomic weight of oxygen, referred to hydrogen as unity.

The density of the principal gases expressed in gms. per c.c. at 0° and under a pressure of 760 mm. of mercury reduced to sea level in lat. 45° is—

	Density.	*Specific gravity referred*		
		to air	*to hydrogen*	*to oxygen* = 16
Air (dry and free from CO_2)	0·0012928	1	14·38	14·47
Oxygen	14290	1·1054	15·90	16·00
Nitrogen (atmospheric, containing argon) .	12568	0·9722	13·98	14·07
Nitrogen (pure) . . .	12507	0·9674	13·91	14·00
Hydrogen	00899	0·06954	1	1·006

The numbers are derived from Lord Rayleigh's experiments, except that for hydrogen, which is from those of Morley and Leduc.

As a rule, however, in molecular weight determinations, it is not necessary to obtain a high degree of accuracy: an accurate equivalent weight is found by gravimetric analysis, and it is only necessary to find whether the molecular weight is equal to this, or twice, three times, four times as great. The problem, whether for gases or vapours, then becomes one within the range of ordinary laboratory practice. An apparatus suitable for measuring the density of gases with an accuracy of about one per cent. has been described by Moissan and Gautier[1], and is shown in Fig. 1 (p. 14). It consists of a gas burette B, into which the gas is driven by the side tube and three-way tap: here it is reduced to atmospheric pressure and its volume and temperature taken. A is a glass bulb of about 100 c.c. provided with a tap, and fitted by a ground-glass joint on to the gas burette. It is weighed full of dry air against a similar bulb as counterpoise, evacuated, and fitted in place as shown; the gas is then allowed to flow into the bulb, and the latter reweighed.

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[1] E. W. Morley, *Ostw.* 17. 87–106 (1895).

§ 2. Molecular Weight of Vapours.

The molecular weight of a vapour can be determined by a measurement of its density, according to Avogadro's law, provided the vapour is not near its point of condensation: when heated some twenty or thirty degrees above the boiling point of the liquid under the pressure used in the experiment, the vapour will usually follow the gaseous laws with sufficient approximation. The exceptions occur when the vapour dissociates. That case requires separate consideration, and it will be seen that vapour density measurements then give valuable information on the course of the dissociation with changes of temperature and pressure. Ordinarily, however, the density of a vapour, when not near saturation, follows Boyle and Charles' laws, so that it always bears the same ratio to the density of hydrogen under the same pressure and temperature. The term specific gravity may conveniently be retained to express that ratio, while density is used in its customary sense of mass per unit volume. As hydrogen is taken to have the unit atomic weight, and is diatomic, its molecular weight is 2, and that of any other gas consequently $= 2 \times$ specific gravity referred to hydrogen (more precisely 2·016 if oxygen be taken as standard, with molecular weight 32).

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[1] Moissan and Gautier, *C. R.* 115. 82-6 (1892).

Of methods for measuring vapour densities, the earliest—that of Dumas—is analogous to the gas-density method. A glass bulb of 100 to 200 c.c. with a long capillary neck is used; it is partly filled with the liquid to be measured, and immersed in a bath of liquid—water, sulphuric acid, or fusible metal, according to the temperature required—at a temperature somewhat above the boiling point of the experimental substance. The vapour formed drives out the air from the bulb, and when all the liquid is evaporated, the end of the neck is fused up, and the temperature of the bath t_2, and pressure of the air p_2, noted. The bulb is then cooled, dried on the outside, and weighed against a similar bulb as counterpoise, giving, say, w_2 grams, a previous weighing of the bulb when full of air giving w_1 as the weight. The point of the bulb is then broken under water, which enters and fills the bulb; the weight W of the latter full of water is then taken. $W-w_1$ is then the volume of the bulb: if p_1 be the pressure and t_1 the temperature of the air with which it was filled during the first weighing, this air weighs

$$(W-w)\frac{273}{273+t_1} \times \frac{p_1}{760} \times 0{\cdot}001293 \text{ gms.},$$

and the empty bulb would weigh w_1 minus this quantity. The weight of the vapour is therefore

$$w_2-w_1+(W-w_1)\ \frac{273}{273+t_1} \times \frac{p_1}{760} \times 0{\cdot}001293.$$

If this be divided by the weight of $W-w_1$ cubic centimetres of hydrogen at t_2 and p_2 the specific gravity will be obtained.

It is sometimes possible to absorb the vapour from the bulb, and estimate its weight by volumetric or gravimetric analysis: this is to be preferred, as it avoids the difficulties of weighing gases directly.

Dumas' method has been used for temperatures above the softening point of glass, with a porcelain bulb: it is, however, not so convenient either for low or high temperatures as that of Victor Meyer.

The principle of this method is to cause the vapour, when generated, to drive out an equal volume of air into a measuring tube. The apparatus consists of a bulb with a long stem about 1 cm. diam. closed at the top by a cork, and carrying near the top a capillary side tube. The bulb and most of the stem are surrounded by a wide jacketing-tube, in which can be boiled water, aniline, or other liquid, to maintain a constant high temperature in the bulb; the side tube either passes into a eudiometer placed in a pneumatic trough (filled with water) or is connected to a gas burette. From one to two decigrams of the liquid to be used are weighed out in a small sealed bulb of glass, which may be placed in a catch in the stem of the apparatus: when the constant temperature—some thirty or forty degrees above the boiling point of the liquid—is attained, the catch is released, the small bulb falls to the bottom of the apparatus and bursts; the liquid evaporates completely in two or three minutes, remaining in the hot part; whilst an equal volume of air is forced into the eudiometer, where its volume pressure and temperature are determined, allowance being made for the fact that it is saturated with water vapour. Then if

v = volume of air,
p = height of barometer in millimetres,

h = height of water in eudiometer above the level outside,

t = temperature of the air,

p_t = saturation pressure of water vapour at t,

w = weight of air,

$$w = 0{\cdot}001293 \times v \times \frac{p - p_t - \frac{h}{13{\cdot}6}}{760} \times \frac{273}{273 + t},$$

and the specific gravity of the vapour (referred to air) is simply got by dividing the weight of liquid used by the weight of air collected. Since air is 14·38 times as heavy as hydrogen, the molecular weight = 14·38 × 2·016 = 28·94 × specific gravity referred to air.

It will be observed that it is not necessary to know the temperature of the bath; it is necessary however to keep it constant, otherwise air will be driven into or out of the measuring tube on account of fluctuations of temperature. Under ordinary circumstances results correct to one or two per cent. can be obtained.

Victor Meyer's method has been applied with success at very high temperatures—even up to 1730° C.—obtained by means of a gas furnace. Bulbs of porcelain or platinum were used, but no important modification of the method was required. In the case of bodies which oxidize easily, the apparatus may be filled with nitrogen or hydrogen, previous to the experiment; and if the substance employed will not volatilize without decomposition under the ordinary pressure, reduced pressure may be employed. In this case a gas-burette rather than a eudiometer should be adopted, and the water in it replaced by mercury.

When high temperatures, obtained by direct application of a flame, are used, it is of interest to know what the temperature in the bulb is. Nilson and Petterson, V. Meyer and others have accomplished this, making use of the bulb itself as an air thermometer, by noting the quantity of air expelled from it whilst heated up from atmospheric temperature to the temperature of the experiment. For details we must refer to the originals[1].

The other chief method, that of Gay-Lussac and Hofmann, may conveniently be described here, although it is not much use for molecular weight determinations. It is capable of much more accuracy than the others, and is suitable for taking measurements over a considerable range of (low) pressures, though only at moderate temperatures on account of the evaporation of the mercury in the working tube, but it is far more elaborate and troublesome to carry out, so that it would never be used in cases in which Victor Meyer's method was available. It consists essentially in placing a weighed amount of liquid at the top of a barometer tube, surrounded by a heating-jacket, and noting the volume, pressure, and temperature of the vapour produced. The pressure exerted by the vapour is measured by the depression of the mercury in the tube, and obviously the pressure must be less than that of the atmosphere. A simple modification, however, allows of a considerable extension in the range of pressures: if the reservoir of the barometer tube be made of strong glass and closed at the top, air may be pumped into it, so that, practically, the experiment may be performed in an artificial atmosphere of pressure equal to a metre, or more, of mercury. This modification is of value when it is desired to trace out the relations between volume and pressure of a fluid, though unnecessary when an ordinary molecular-weight determination is in question. The accompanying figure (Fig. 2), taken from a paper by S. Young and G. L. Thomas[2], shows the modified apparatus. It consists of a mercury reservoir E, in which dips the barometer tube A, which is graduated

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[1] Langer and V. Meyer, *Pyrochemische Untersuchungen*, Braunschweig, 1885.

[2] *Proc. Phys. Soc.* 13. 659 (1895).

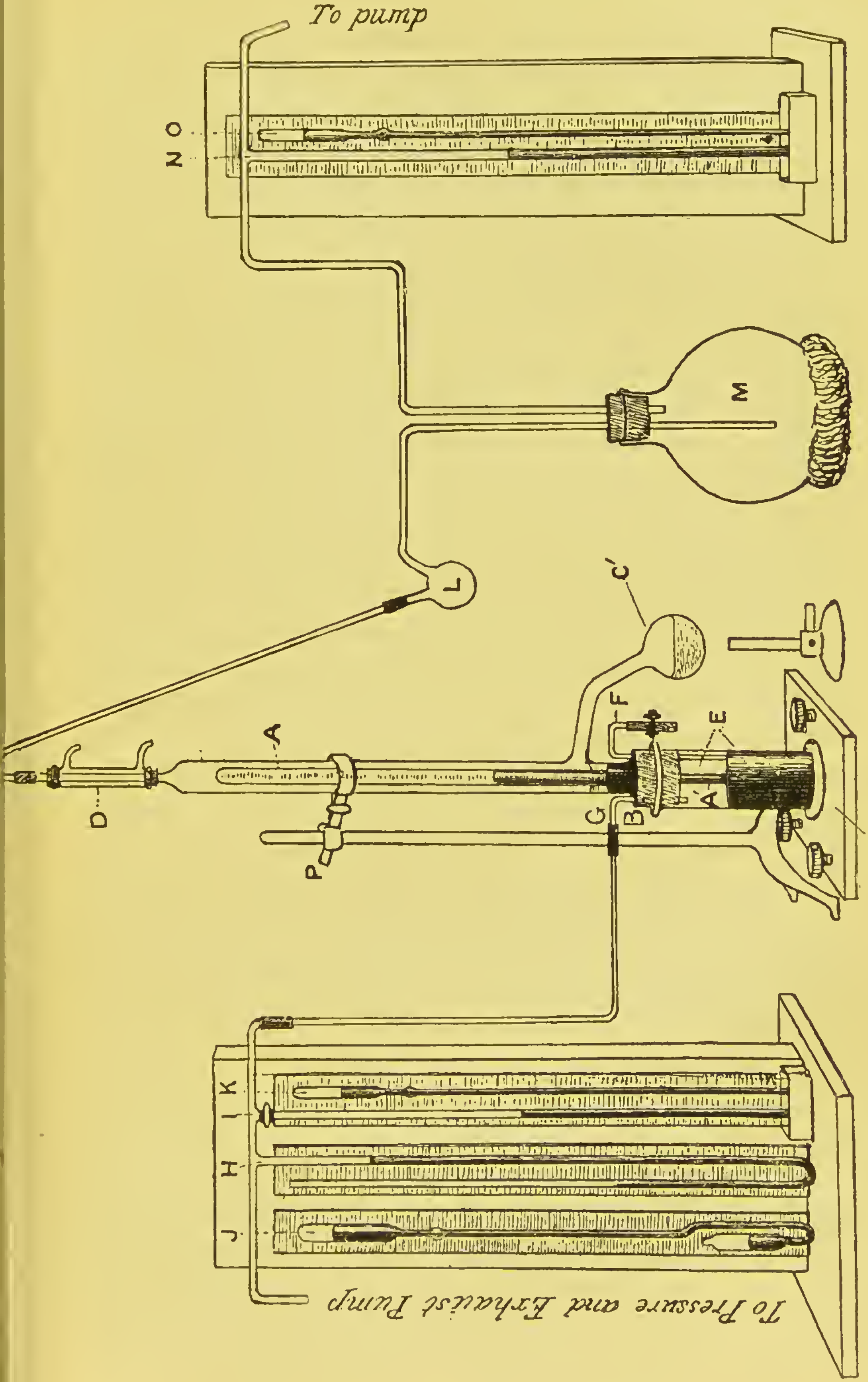

FIG. 2.

in millimetres throughout its length, and is wide for the greater part of its length, in order to hold a greater mass of vapour. Pressures are read off it directly, and have to be corrected for the temperature to which the mercury column is raised; for the measurement of volume, the tube is previously calibrated. The tube fits through a rubber cork, which also supports the jacket C. The upper part of A is connected through a side tube G with a pump and gauge J H K, so that the air in A may be brought to a higher or lower pressure as desired, and the pressure measured. The jacket is of the pattern recommended by Ramsay and Young, allowing the liquid in C′ to be boiled under reduced pressure: D is a short reflux condenser, M a reservoir of air to keep the pressure more steady, and NO a mercury gauge. This method of jacketing is a most convenient one for many purposes, as by the choice of a few stable liquids easily obtained pure, it is possible to produce any required temperature up to 350° and maintain it indefinitely. Ramsay and Young[1] prepared a set of tables showing the temperatures corresponding to certain vapour pressures of carbon disulphide, alcohol, chlorobenzene, bromobenzene, aniline, methyl salicylate, bromonaphthalene, and mercury. To obtain a given temperature, choose the most appropriate of these liquids, and placing it in the jacket, reduce the pressure to that quoted in the tables for the temperature required; on heating the bulb C′ the liquid will boil and maintain this temperature in any apparatus the jacket encloses.

§ 3. Molecular Weight in Solutions: Osmotic Pressure.

Of late years great advances have been made in the direction of measuring the molecular weight of bodies in the liquid form. The results obtained for pure liquids are still open to considerable doubt, as the methods by which they are obtained are either lacking in generality or insufficiently clear from the theoretical standpoint, but for the highly important class of solutions molecular weights may be regarded as known with as much precision as for gases. This is due chiefly to the analogy drawn by van 't Hoff between *dilute solutions* and gases. From the point of view of the molecular theory, the properties of gases are simply explained by the relative freedom from interaction of gaseous molecules. In a liquid, the molecules, though moving with considerable velocity and freely changing their relative positions, are nevertheless so closely packed that they are always either in contact with neighbouring molecules, or at least near enough to suffer appreciable forces of attraction and repulsion from them; but when a liquid is vapourized under the customary pressure, it expands something like a thousand-fold, so that the average distance between two adjacent molecules in any direction is increased tenfold. Now the forces between molecules fall off very rapidly indeed as the distance between them increases, so that in such a vapour they are almost negligible. It follows that the properties of a vapour or gas can be calculated from a consideration of its molecular movements alone; in other words, by considering the kinetic energy of the molecules, neglecting any potential energy the substance may possess on account of internal attractions and repulsions. The result of such calculation is in accordance with the laws of gases as derived from observation, viz. (1) the pressure exerted by a gas is proportional to the number of molecules per unit of volume (i.e. proportional to the density) (Boyle); (2) regarding the absolute temperature as being the expression of the *mean kinetic energy of translation of a molecule* (therefore proportional to the square of the mean velocity), the pressure of a gas is proportional to its absolute temperature (Charles and Gay-Lussac). The exact result is that the pressure may be put $= \frac{mnu^2}{3}$, where m = mass of a molecule, n = number of molecules per c.c., u = mean velocity[1]. Now $m \times n$ = mass of 1 c.c. of the gas, so that $\frac{mnu^2}{2}$ is the kinetic energy of translation of the molecules (apart from any kinetic energy they may possess on account of rotations, internal vibration, &c.). It follows that the pressure of a gas is numerically equal to two-thirds of the kinetic energy of translation of its molecules. This result holds for all gases, so that if any two gases have the same pressure they must have the same amount of kinetic energy of translation per c.c.; but if they also possess the same temperature, the product $\frac{mu^2}{2}$ is the same for each: hence in two gases at the same temperature and pressure n, the number of molecules in unit volume is the same (Avogadro).

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[1] *J. C. S.* 47. 640–57.

Now the molecules of a substance in solution are capable of producing an effect—known as osmotic pressure—between which and gaseous pressure a very close analogy exists. To show osmotic pressure it is necessary first to find a material which is permeable for the solvent but not for the dissolved substance. Such semi-permeable membranes occur commonly in the tissues of animals and plants, and they have been constructed artificially, the best known form being the precipitate produced at the surface of contact of a solution of copper sulphate with one of potassium ferrocyanide.

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[1] Properly speaking, the square root of the mean square velocity: got by dividing the sum of the squares of the velocity of each molecule by the number of molecules, and then extracting the square root, or $u = \sqrt{\frac{\Sigma(u_1^2 + u_2^2 + u_3^2 + \ldots)}{n}}$, where u_1, u_2, u_3, &c., are the velocities of the individual molecules. This is not the same thing as the true mean velocity $= \frac{\Sigma(u_1 + u_2 + u_3 + \ldots)}{n}$.

The copper ferrocyanide membrane is freely permeable for water, but practically impermeable for substances with high molecular weights, such as sugar. An osmotic cell, then, may be constructed according to the directions of Pfeffer[1] by filling a porous earthenware jar with sugar solution, containing a little copper sulphate, and immersing it in a dilute solution of ferrocyanide; the semi-permeable membrane will be formed in the interior of the earthenware. The molecules of sugar, being separated somewhat widely by the water in which they are dissolved, are free from one another's influence in the same sense as gas molecules are, and will produce a pressure on the walls of the containing vessel. Now the only way in which the sugar solution can expand is by drawing water from the outer vessel through the membrane: that will accordingly take place, and constitutes the phenomenon known as osmosis. The level of liquid inside the cell will rise above that outside, and will continue to rise until the pressure due to the liquid column, thus set up, balances the osmotic pressure in the cell. In carrying out the experiment it is convenient to fit the earthenware cell with a cork, through which passes a narrow upright glass tube, and to immerse the cell in a large mass of water; the rise of liquid in the narrow tube will then produce equilibrium before so much water is drawn in as to alter sensibly the concentration of the sugar solution, and in this way the osmotic pressure of solutions of varying strength can be measured. If the pressure is considerable—and it may amount to several atmospheres—the top of the narrow tube may be connected to a compressed-air manometer instead of being left open to the air. The results obtained in this way are thoroughly in agreement with van 't Hoff's theory, showing that the osmotic pressure follows the laws of Boyle, Charles, and

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[1] *Osmotische Untersuchungen*, Leipzig, 1877. Cf. also Ramsay, *Ostw.* 15. 518.

Avogadro; the number of molecules per c.c., which in the case of gases is represented by the density, being here represented by the 'concentration,' i.e. the mass of dissolved substance in a unit of volume of the solution. The concentration of solutions is, as a matter of fact, expressed in several different ways, each of which is convenient, according to circumstances. Thus it may be expressed in grams per 100 gms. of solvent, or in grams per 100 gms. of the solution. If C_1 stand for the first of these quantities, and C_2 for the second, then

$$C_2 = C_1 \times \frac{100}{100 + C_1}.$$

In dealing with the osmotic pressure, however, it is more convenient to express the concentration in volume. Thus, if C_3 mean the mass in gms. of dissolved substance per 100 c.c. of solution, and D be the density of the solution,

$$C_3 = C_2 \times D.$$

Still more convenient is the mass in gram-molecules per unit volume, usually in this case the litre. If C_4 be this last quantity,

$$C_4 = 10 C_3 \div M,$$

where M is the molecular weight of the dissolved substance.

Further, we may in cases find it convenient to express the concentration of the solution by the ratio of the number of molecules of dissolved body to the number of molecules of solvent, either by stating the number of the latter for one of the former, or by the fraction the former is of the total number. The latter quantity, C_5, is the *molecular fractional concentration*, and

$$\frac{C_5}{1 - C_5} = \frac{C_2 \div M}{(1 - C_2) \div m},$$

where m is the molecular weight of the solvent.

Adopting the fourth meaning for the concentration—gram-molecules per litre—it is clear that two solutions will have the same concentration when they contain the same number of molecules in unit volume, and therefore possess the same osmotic pressure (at the same temperature).

Pfeffer found for solutions of sugar in water

Concentration.	*Osmotic pressure.*	*Press. ÷ conc.*
1 %	53·5 cm.	53·5
2	101·6	50·8
2·74	151·8	55·4
4	208·2	52·1
6	307·5	51·3

These numbers are, considering the difficulty of the experiment, a satisfactory confirmation of Boyle's law, as applied to solutions; while, as regards temperature variation, he found for a 1 per cent. solution

Temp.	*Osmotic pressure.*
6.8	50·5 cm.
22·0	54·8
36·0	56·7

numbers which are very fairly represented by the equation

$$p = 49{\cdot}3 \times \frac{(273+t)}{273}.$$

Far more evidence has, however, been accumulated by means of indirect measurements of the osmotic pressure, which we shall have to consider later. Manipulation of semi-permeable membranes is difficult, and their impermeability to dissolved substances is by no means perfect, and the method has been but rarely used. Another method in which direct use is made of osmotic pressure and living cells form the means of observation has met with rather more applications. A living plant-cell, a blood corpuscle, or a bacterium, consists of a layer of protoplasm containing the sap or fluid of the cell; the sap is a moderately strong solution of various salts and other soluble substances, mostly organic, and has a very appreciable osmotic pressure. The enclosing protoplasm acts as a semi-permeable membrane, so that when the cell is immersed in water it keeps taut.

If the cell is exposed to the air, evaporation may diminish the contained water so that it no longer possesses sufficient rigidity—as when a plant droops for want of rain. If the cell be placed in a solution of osmotic pressure greater than its own, a similar phenomenon, known as plasmolysis, is observed, water being withdrawn osmotically from the cell-sap, so that the cell shrinks. De Vries[1] and others have in that way compared the osmotic strength of various substances by observing the least concentration of each required to plasmolyze living cells. For instance, the concentrations (expressed in gram-molecules) required to produce the same osmotic effect were

Glycerine,	$C_3H_8O_3$	. . . 1·78
Laevulose,	$C_6H_{12}O_6$	. . . 1·88
Cane-sugar,	$C_{12}H_{22}O_{11}$	. . . 1·81

—practically identical, showing that the molecular weights do correspond to the chemical formulae given.

All these results may be summarized by saying that dilute solutions, like gases, follow the characteristic equation

$$PV = RT,$$

where P now means the osmotic pressure, and V the 'dilution' (reciprocal of the concentration), i. e. the volume occupied by one gram-molecule of the dissolved substance. If P be in dynes per sq. cm., and V in c.c., the value of R, as shown in the introduction, is 83,157,000. Thus, for example, a solution contains 1 gm. of cane-sugar in 100 gms. —therefore 100 c.c.—of water. The molecular weight of sugar is 342, so that the volume containing 1 gm. mol. is 34,200 c.c.; hence

$$P = 83{,}157{,}000\, T \div 34{,}200.$$

At 22° centigrade, i. e. $T = 273 + 22$, this gives

$$P = 712{,}000 \text{ C. G. S. units} = 0·712 \text{ atmos.}$$

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[1] De Vries, *Ostw.* 2. 414; Hamburger, l.c. 6. 319.

Pfeffer, as mentioned above, found $P = 54{\cdot}8$ cms. of mercury or $54{\cdot}8 \div 75 = 0{\cdot}731$ atmos.

Since the osmotic pressure of a solution tends to attract and retain water in the solution, it will offer a resistance to any process which tends to remove water. Evaporation and refrigeration are such processes, and accordingly the tendency to the formation of vapour or ice from a liquid will be lessened by the solution in it of a substance that will not itself evaporate or crystallize out; in other words, the boiling point of the liquid will be raised, and its freezing point lowered. The alteration may be considered quantitively in the following way.

§ 4. Vapour Pressure of Solutions.

Imagine an osmotic cell, such as used by Pfeffer, provided with a vertical gauge tube, open at the top, the whole being placed in an enclosure free from air so that the enclosure may become saturated with vapour, and let the whole be maintained at a constant temperature.

Then the liquid both inside and outside the porous cell will eventually come into equilibrium with the vapour. But the pressure on the two liquid surfaces is not the same; for the solution inside the cell is at a higher level, by h cms. say, than the solvent outside; consequently the vapour pressure on the solution is less than that on the solvent by the pressure of a column of vapour h cms. high. This will be made plainer, perhaps, by the following argument: suppose the saturation pressure of solvent and solution were the same; then, if the vapour pressure in the receiver be in equilibrium with the solvent, it will, h cms. higher up, be below the saturation pressure of the solution; some of the solution will therefore evaporate, and the pressure in the receiver will rise. The pressure of the vapour in contact with the solvent will become too high, and condensation will occur there; in other words, distillation from the inside to the outside of the cell will take place. Now the solution will in this way become stronger, and so will attract water osmotically through the semi-permeable membrane, so that a cyclical process will be set up, which would go on of its own accord for ever. It is almost obvious that such a state of things could not occur; it would, moreover, be in formal contradiction with the second law of thermodynamics (see chap. iii). We are thus led by a *reductio ad absurdum* to the above conclusion as to the difference between saturation pressures of solvent and solution, viz.

$$p_1 - p_2 = ghd,$$

where $p_1 =$ saturation pressure of solvent at T,
$p_2 =$ saturation pressure of solution at T,
$g =$ acceleration of gravity $\left(= \frac{981 \text{ cm.}}{\text{sec}^2}\right)$,
$h =$ height of osmotic cell,
$d =$ density of vapour;

or as we may more conveniently write it

$$p_1 - p_2 = \frac{ghm}{v_1},$$

where $m =$ molecular weight of the solvent in form of vapour,
$v_1 =$ molecular volume of the vapour of solvent.

Now since the osmotic pressure follows the same laws as the gas pressure, we have

$$p_1 v_1 = PV = RT,$$

where V is the molecular volume (or dilution) in c.c. per gm. of the dissolved substance. Hence

$$p_1 - p_2 = \frac{ghmp_1}{PV};$$

but the osmotic pressure $P = ghD$, where D is the density of the liquid (practically the density of the solvent, since the solutions are supposed dilute). Hence

$$\frac{p_1-p_2}{p_1}=\frac{ghM}{PV}=\frac{ghM}{ghDV}=\frac{M}{DV};$$

but $\frac{D}{M}$ is the number of gram-molecules of solvent in unit volume, while $\frac{1}{V}$ is the concentration, i.e. number of gram-molecules of dissolved substances in unit volume: so we arrive at the simple rule

$$\frac{p_1-p_2}{p_1}=\frac{\text{number of molecules of dissolved substance}}{\text{number of molecules of solvent}}.$$

The quantity $\frac{(p_1-p_2)}{p_1}$ is called the 'relative lowering of vapour pressure.' The rule with regard to it was found empirically by Raoult.

[The above argument is somewhat inexact, mathematically. It should refer to the infinitesimal change of vapour pressure due to an infinitesimal change of concentration in the solution, and lead to an expression for $\frac{dp}{p}$ instead of $\frac{(p_1-p_2)}{p_1}$, which, when integrated, gives $\log p_1-\log p_2=\frac{M}{DV}=$ ratio of numbers of molecules of dissolved substance to those of solvent. The difference is, however, inappreciable unless the solution is very strong. Thus a 10 per cent. sugar solution contains 1 gm. molecule of sugar in 3,420 gms. of water, i.e. in 190 gm. molecules of water: it should therefore depress the vapour pressure by $\frac{1}{190}$ part. If we take the effect at the ordinary boiling point, the pressure 760 mm. for pure water becomes 756 for the solution. The exact formula,

$$\log p_1-\log p_2=\tfrac{1}{190}$$

(remembering that the logarithms are 'natural' or 'Napierian'), gives $p_2=756{\cdot}01$ mm., so that even in this case it is practically unnecessary to use it.]

Since the relative lowering of vapour pressure depends only on the ratio of the number of molecules present, it is independent of the temperature—except in cases where the molecular weight varies with temperature on account of dissociation.

It is essential to remark that in the preceding theory, although M, the molecular weight of the dissolved substance, refers to that substance in the liquid state (producing osmotic pressure), m, the molecular weight of the solvent, refers to the solvent in the gaseous state (being derived from vapour pressure measurements), and no assumption is made that the liquid solvent is in the same molecular condition as its vapour. Neglect of this point has led to the erroneous opinion that by observations of lowering of vapour pressure (and rise of boiling point, lowering of freezing point, &c.) information could be obtained on the molecular weight of the solvent in the liquid state.

§ 5. Boiling Point of Solutions.

The above relation may be regarded on the basis of a method for determining molecular weights, for if the molecular weight of the dissolved body be unknown, the equation gives the means of calculating it from observation of the vapour pressure of its solutions. It is not customary, however, to make use of it directly, but to determine the rise in boiling point of the solvent due to dissolution of solid in it, which is the necessary correlative of lowered vapour pressure.

The connexion between the two may be found by means of the equation

$$\log p = -\frac{ml}{RT} + \text{constant},$$

which represents the change of saturation pressure with temperature. l is the latent heat of evaporation of the solvent, and M its molecular weight. This equation, which is derived from thermodynamical reasoning, and is verified by experiment, will have to be considered later: at present we must assume it, and make use of it to evaluate the osmotic pressure.

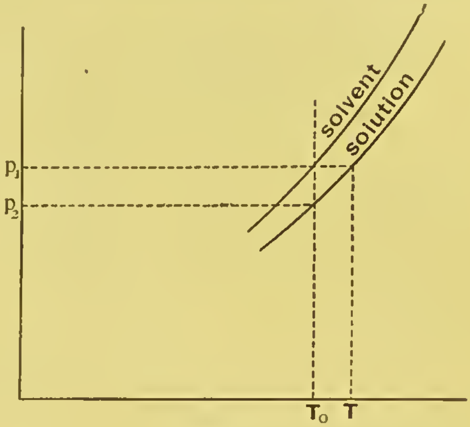

Fig. 3.

Now if at temperature T_0 the solvent have a vapour pressure p_1 but the solution p_2, then at a slightly higher temperature T the solution will have a vapour pressure p_1, and $T-T_0$ is the extent to which the boiling point—under pressure p_1—is raised by the dissolution of the solid. Applying the above equation, since

$$\log p_1 = -\frac{ml}{RT} + \text{constant},$$

and

$$\log p_2 = -\frac{ml}{RT_0} + \text{constant},$$

by subtraction

$$\log p_1 - \log p_2 = \frac{ml}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right),$$

or, writing t for the rise of boiling point,

$$\log p_1 - \log p_2 = \frac{mlt}{RT_0T}.$$

To get the osmotic pressure in terms of the change of vapour pressure, we have, by the previous reasoning on the osmotic height, that

$P : p_1 - p_2 ::$ density of solution : density of vapour,

or

$$P = \frac{(p_1-p_2)D}{d};$$

but the density of the vapour $= \dfrac{m}{v}$, where v as usual is the molecular volume, and this by the characteristic equation is $= \dfrac{mp}{RT}$. Hence

$$P = \frac{p_1 - p_2}{p} \cdot \frac{RTD}{m} \quad \text{or} \quad \frac{p_1 - p_2}{p} = \frac{mP}{RTD}.$$

For the same reason as before, the fraction $\dfrac{(p_1 - p_2)}{p}$ representing the relative lowering of vapour pressure should, exactly, be
$$\log p_1 - \log p_2 = \frac{mP}{RTD}.$$

Combining this with the result just found for the change in boiling point, we have

$$\frac{mP}{RTD} = \frac{mlt}{RT_0T} \quad \text{or} \quad P = \frac{ltD}{T_0}.$$

As examples of this result take for aqueous solutions:

$l = 536{\cdot}4$ calories $= 536{\cdot}4 \times 42{,}000{,}000$ ergs;
$D = 0{\cdot}959$ (at the boiling point);
$T_0 = 273 + 100.$

Hence $\quad P = \dfrac{536{\cdot}4 \times 42{,}000{,}000 \times 0{\cdot}959}{373} t$

$= 57{,}900{,}000t$ dynes per sq. cm. $= 57{\cdot}9t$ atmospheres; i.e. a rise of one degree in the boiling point implies an osmotic pressure of 57·9 atmos.

For benzene, the latent heat being much smaller, the change of boiling point is much greater.

$l = 93{\cdot}4$ calories;
$D = 0{\cdot}815$;
$T = 273 + 80$;

$$P = \frac{93{\cdot}4 \times 42{,}000{,}000 \times 0{\cdot}815}{353} t$$

$= 9{,}060{,}000t$ in C. G. S. units $= 9{\cdot}06t$ atmospheres.

Returning to the practical problem of determining molecular weights, we may use the elevation of the boiling point instead of the depression of the vapour pressure. Suppose a solution contains one gram-molecule of solid in 100 gms. of solvent, therefore in $\frac{100}{D}$ cubic centimetres. Substituting this value of V in the characteristic equation

$$PV = RT,$$

we have
$$P = \frac{RTD}{100};$$

but since
$$P = \frac{ltD}{T},$$

it follows that in this case

$$t = \frac{RT^2}{100l} = t_m, \text{ say,}$$

where t_m is the quantity called by van 't Hoff the 'molecular elevation of the boiling point';

$$R = 83{,}157{,}000 \text{ ergs.} = 1{\cdot}9845 \text{ calories,}$$

and since l is always expressed in calories, we must adopt the same unit in the numerator and write

$$t_m = \frac{0{\cdot}019845\,T^2}{l} \text{ or } = \frac{0{\cdot}02\,T^2}{l} \text{ nearly.}$$

If an experiment made with x grams of an unknown substance to 100 gms. of solvent give a rise of boiling point t, then

$$\frac{\text{molecular weight}}{x} = \frac{t_m}{t}.$$

The method of determining molecular weights by the boiling point of solutions, as well as that by the freezing point, has come to be associated with the name of Beckmann, since he has worked out its practical details to the most minute point, and his form of apparatus has been almost universally adopted. The latest form[1] of it is shown in Fig. 4. It consists of the boiling tube A provided with two side tubes t_1 t_2. t_1 serves for the introduction of the

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[1] Beckmann, *Ostw.* 21. 246.

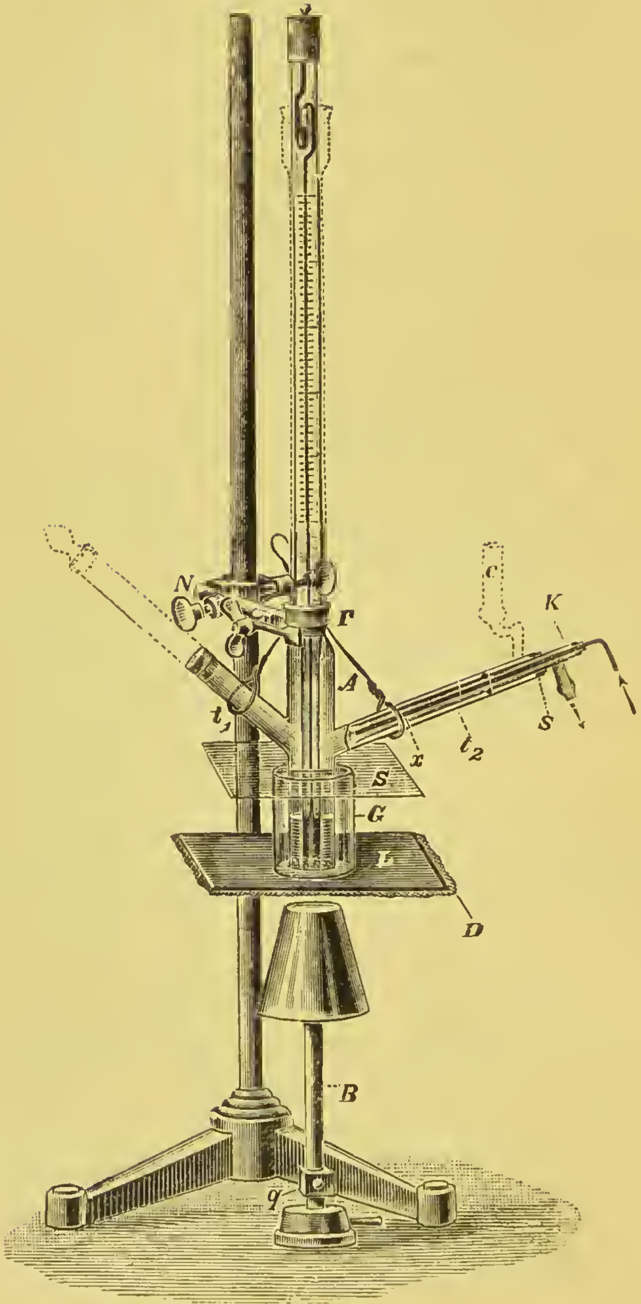

FIG. 4.

substance, t_2 carries a condenser K. The boiling tube stands on a sheet of asbestos L and a piece of wire gauze D; it is also supported by a clamp N. As an air-jacket to the boiling tube, the open cylinder of glass G is placed round it, and surmounted by a sheet of mica S. C is a calcium chloride tube, to be used with hygroscopic materials or when the cooling water in the condenser would cause a deposition of dew. The condenser may be dispensed with in case of liquids boiling above 100°. Rising vertically from the boiling tube is the thermometer, of special construction. As it is only intended to indicate small differences of temperature, it is made with a very large bulb, and the scale, extending over a few degrees only, is divided (usually) into hundredths of a degree; but to make the same thermometer available for the boiling point of various solvents, such as benzene, ethylacetate, acetic acid, &c., a small bulb is provided at the top: by appropriate heating and shaking more or less of the mercury can be separated and stored in this bulb, so that the mercury in the stem when at the desired temperature is at a convenient level on the scale. The solvent may be introduced by a pipette, or weighed out in the boiling tube, which can be hung to the arm of a balance; there must be enough of the liquid to cover the thermometer bulb, for which purpose 10 c.c. suffices. The substance to be dissolved may conveniently be introduced, if solid, in the form of a small pastille, shaped in a steel press; if liquid, by means of a small pipette somewhat similar in shape to a Sprengel pyknometer. The liquid will not boil freely, and impart a constant temperature to the thermometer, unless some such material as glass beads, or platinum foil, be placed in the boiling tube. According to Beckmann, some 10 to 20 grams of platinum foil bent into small tetrahedra works most satisfactorily. If then the flame be carefully adjusted, and the liquid be boiled for about half an hour, the reading of the thermometer will become constant to $\frac{1}{100}$°. The boiling point of the solvent is thus measured on the arbitrary scale of the thermometer; a weighed quantity of the substance introduced, and after a few minutes the boiling point again observed, in order to determine the difference t.

The value of the molecular elevation, t_m, for various solvents is as follows (Ostwald):—

Ether	21·1	Ethyl acetate	26·1
Benzene	26·7	Acetone	16·7
Chloroform	36 6	Water	5·2
Carbon disulphide	23·7	Ethylene dibromide	63·2
Acetic acid	25·3	Aniline	32·2
Ethyl alcohol	11·5	Phenol	30·4

As an instance of the calculation of the results, we will take the following experiments from Beckmann's work:—

9·0464 gms. cane-sugar dissolved in 41·73 gms. of water raised the boiling point 0·317°. Here x, the percentage of sugar, = 21·68.

The molecular weight is therefore

$$= \frac{xt_m}{t} = 21·68 \times \frac{5·2}{0·317} = 358 \text{ (while } C_{12}H_{22}O_{11} = 342\text{)}.$$

Again, 1·5997 gm. anthracene in 56·74 gms. benzene raised the boiling point 0·408°. $x = 2·82$ per cent.

$$\text{Molecular weight} = 2·82 \times \frac{26·7}{0·408} = 185$$

(while $C_{14}H_{10} = 178$).

§ 6. Freezing Point of Solutions.

If from a solution some of the solvent be frozen out, since the volume is diminished, the osmotic pressure of the remaining solution is increased; thus the osmotic pressure tends to resist the freezing, and the freezing temperature will be lower than that of the pure solvent. The extent of the lowering may conveniently be calculated by means of the rise of boiling point for which we have already found an expression.

Now the melting point of a substance means the temperature at which two modifications of it, the solid and liquid, exchange stability. Below it, the solid is the more stable, but the liquid is capable of existing; it is then in the state known as 'undercooled,' and a slight disturbance is sufficient to make it assume the more stable solid form. Above the melting point the liquid becomes the more stable, and the solid has not been obtained; but in precisely analogous cases of chemical conversion, e. g. of rhombic into monosymmetric sulphur at 95·6°, it is possible to obtain both forms at temperatures both below and above the conversion point; only below 95·6° the rhombic form is the more stable, while above that temperature the monosymmetric form is the more stable.

These relations are well brought out if we consider the equilibrium of solid and liquid with their vapour. The liquid has a definite saturation pressure corresponding to any temperature, and the curve connecting the two quantities can be traced out a good many degrees below the normal freezing point. The solid also sublimes at a definite pressure, varying with the temperature; and the variation of this can be traced out at temperatures below the freezing point. Thus, for example, for benzene it has been found that:—

Temp.	*Saturation pressure over*	
	liquid.	*solid.*
0°	26·6 mm.	24·61
1°	28·1	26·31
2°	29·65	28·17
3°	31·3	30·18
4°	33·06	32·34
5°	34·93	34·64
6°	36·69	

If these numbers be plotted on a diagram they will give two curves convex to the axis of temperature, ADB for the liquid, CD for the solid. It will be noticed that CD lies below ADB, but rising more steeply cuts the latter at D, and if prolonged would lie above the line for the liquid. *The state with lower vapour pressure is in each case the more stable*, so that CD and DB form the boundary of the vapour, while the dotted curve AD represents an equilibrium between undercooled liquid and vapour which is unstable. At the pressure and temperature represented by D the liquid is in equilibrium with the vapour, and so is the solid, consequently liquid and solid are in equilibrium with one another. D is the so-called 'triple point,' the only condition in which solid liquid and vapour can all be present together; it is clearly the melting point of benzene under a pressure equal to that of the saturated vapour. The numbers quoted above give for D a pressure of 36·06 mm. and a temperature 5·58°. The melting point under atmospheric pressure will be nearly the same as this, but not quite, for the melting point is raised slightly by increase of pressure.

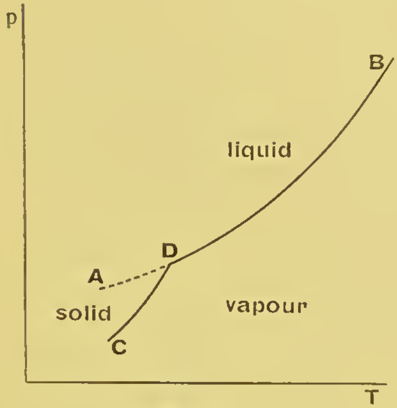

FIG. 5.

Now a relation between the sublimation pressures exists, similar to that previously quoted, between the evaporation pressures. (See Fig. 6.)

Thus, if T_0 = freezing point of solvent,
T = freezing point of solution,
p_0 = vapour pressure of either ice or solvent at T_0,
p_1 = vapour pressure of solvent at T,
p_2 = vapour pressure of ice at T,
l_1 = latent heat of evaporation of solvent,
l_2 = latent heat of sublimation;

$$\log p_0 - \log p_1 = \frac{ml_1}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

$$\log p_0 - \log p_2 = \frac{ml_2}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where, as usual, m is the molecular weight (of solvent) R the gas constant. Hence

$$\log p_1 - \log p_2 = \frac{m(l_2 - l_1)}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

and we may put $l_2 - l_1 = l_3$, the latent heat of fusion of ice, since, in order to convert ice into vapour, it might either be sublimed direct, with an expenditure of heat l_2, or first melted and then evaporated, in which case the same quantity of heat would be divided into the two portions l_3 and l_1. Hence

$$\log p_1 - \log p_2 = \frac{ml_3}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right).$$

Now p_2 is also the vapour pressure of the solution at T, for that is the point at which ice separates out from it, and ice and solution are simultaneously in presence of the vapour. Hence the last equation shows the relation between the pressures of solution and solvent at the same temperature T.

But we have seen that the osmotic pressure P is connected with the vapour pressures by the equation

$$\log p_1 - \log p_2 = \frac{mP}{RTD},$$

where D = density of the solution (or solvent, since the solution is dilute).

Therefore $$\frac{mP}{RTD} = \frac{ml_3}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

or $$P = \frac{l_3 D}{T_0}(T_0 - T) = \frac{l_3 D}{T_0} t, \text{ say,}$$

where t is the lowering of freezing point corresponding to the osmotic pressure P. It should be noticed that this expression is precisely similar in form to that previously given for the relation between osmotic pressure and change of boiling point.

For example, if water is the solvent, the osmotic pressure per degree lowering of freezing point is

$$\frac{P}{t} = \frac{80{\cdot}0 \times 42{,}000{,}000 \times 1{\cdot}000}{273} = 12{,}310{,}000 \text{ C. G. S. units}$$
$$= 12{\cdot}31 \text{ atmos.}$$

For benzene, the heat of fusion being 30·08 and the density 0·8875,

$$\frac{P}{t} = \frac{30{\cdot}08 \times 42{,}000{,}000 \times 0{\cdot}8875}{273 + 5{\cdot}5} = 4{,}026{,}000 \text{ C. G. S. units}$$
$$= 4{\cdot}026 \text{ atmos.}$$

Thus the freezing point of a one per cent. sugar solution has been found to be $-0^{c}{\cdot}059$, giving an osmotic pressure of 0·73 atmos. or 54·4 cm. of mercury (calculated pressure 49·4).

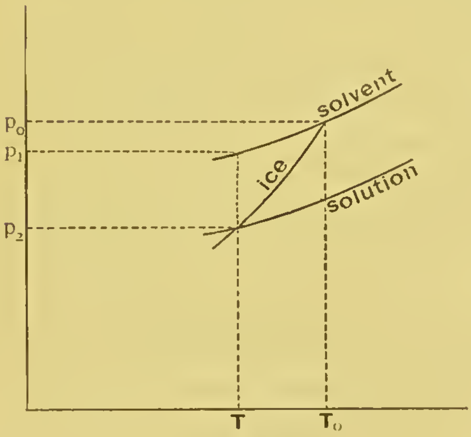

FIG. 6.

The freezing-point method has shown itself in practice to be the most convenient method of determining the osmotic pressure, and therefore the molecular weight in solutions. As in the case of the boiling point, if one gram-molecule of a substance is dissolved in 100 grams of solvent, and therefore in $\frac{100}{D}$ cubic centimetres, the characteristic equation $PV = RT$ gives

$$P = \frac{RT_0 D}{100} = 0{\cdot}019845\, T_0 D\,;$$

but since $P = \frac{l_3 D t}{T_0}$, it follows that the depression t, which in this case may be written $t_m, = \frac{0{\cdot}019845 T_0^2}{l_3}$. This quantity is the 'molecular depression of the freezing point.' If then an experiment be made with x grams of an unknown substance to 100 gms. of solvent, and give a depression of t degrees,

$$\frac{\text{molecular weight}}{x} = \frac{t_m}{t}.$$

§ 7. Practice of the Freezing-point Method.

The apparatus for determinations by the freezing-point method also is commonly used in the form given to it by Beckmann. It consists of a stout test-tube A (Fig. 7) with a side tube which serves conveniently to introduce the materials. It is closed at the top by a cork carrying the thermometer, of the same pattern as for boiling-point observations, and allowing room for a stirrer, preferably of platinum with a glass handle. For use with acetic acid or other hygroscopic solvent, Beckmann[1] has described a stirrer consisting of a gilt iron ring with platinum wires depending from it, lifted up and down by the action of an electromagnet through which an intermittent electric current is passed. With such a device the apparatus can be completely closed against damp, and with it, or any mechanical stirrer, more constant results are obtained than with hand stirring. The test-tube is fitted by a cork into a shorter and wider tube B, which serves as air-jacket to prevent too rapid changes of temperature. This again is supported by the lid of the beaker C, in which is contained the ice or freezing mixture, &c., required to freeze the solution. To make an experiment then, enough of the liquid to cover the bulb of the thermometer is weighed out in the test-tube, or introduced by a pipette: about 10 c.c. being necessary. The test-tube without its jacket is then inserted into the freezing mixture and left till the solvent begins to freeze; it is then removed, wiped, placed in the jacket and the stirrer set working, and after sufficient constancy is attained, the thermometer is read. The test-tube is then removed, and the substance to be dissolved introduced and dissolved by stirring, the stirring being kept up till almost all the ice has melted. The test-tube is then replaced and its temperature allowed to fall a degree or so below the freezing point of the solution: on working the stirrer ice crystallizes out and the thermometer rises to the freezing point of the solution, which is then read.

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[1] *Ostw.* 21. 241 (1896).

The molecular depression for the most common solvents is as follows (Ostwald):—

Water . . .	18·9	Benzene . . .	49·0
Acetic acid . .	38·8	Phenol . . .	75·0

As a specimen of the results obtained we may quote an experiment in which 2·47 grams of ethyl benzoate were dissolved in 100 of benzene. The lowering of the freezing point was found to be 0·840°. Hence the molecular weight was calculated as—

$$2{\cdot}47 \times 49{\cdot}0 \div 0{\cdot}840 = 144 \ (C_6H_5COOC_2H_5 = 150).$$

Much attention has been paid to the freezing-point method, not merely in order to verify molecular weights, for which purpose a very moderate degree of accuracy is sufficient, but also to determine the actual value of the osmotic pressure. Here it is clearly necessary to get as accurate results as possible, since the object is to test the theory put forward by van 't Hoff, according to which osmotic pressure may be calculated in the same way as gas pressure. The laws of gas pressure themselves (Boyle's and Gay Lussac's) are only approximate, and so no doubt are those relating to the osmotic pressure; and only by experiment is it possible to find out with what degree of exactness they hold. In order to make a freezing-point determination as exact as possible, it is necessary to pay attention on the one hand to the establishment of the equilibrium of temperature aimed at, and on the other to the instrument used to measure it. The precautions to be taken on the latter point are very much the same as in any exact thermal work —calibration of the thermometer scale, study of the change of zero point, &c.: we must refer to the memoirs on freezing-point determinations, or to the treatises on heat. The question of establishing the temperature equilibrium is of more theoretical interest. Nernst[1] was the first to point out that the steady temperature assumed by a thermometer placed in water containing melting ice is not in general the temperature of the ice. If a mass of liquid be placed in the freezing apparatus, and be exposed to the various influences which tend to change its temperature—radiation to the freezing mixture, radiation from the warmer objects in the room, warming by the air, by the action of the stirrer—it will, in the absence of any solidification of the mass, tend to assume a certain equilibrium temperature, called by Nernst the 'convergence temperature.' This may, according to circumstances, be above or below the true freezing point. Now the liquid will, if

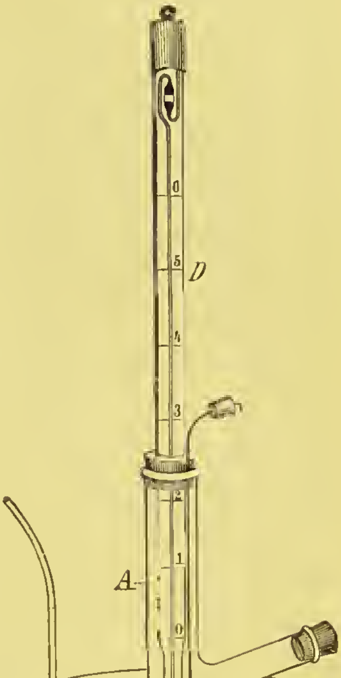

Fig. 7

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[1] W. Nernst and R. Abegg, *Ostw.* 15. 681–93 (1894).

undercooled as usual in the experiment, be driven towards the freezing point at a certain rate, depending on the rate with which ice separates out from it; but it will also be driven towards the convergence temperature at a rate depending on the various external circumstances. The temperature it finally assumes therefore, and that read by the thermometer, will be a compromise lying between the freezing and converging temperatures. In order to make this 'apparent freezing point' differ as little as possible from the true one, it is necessary (1) to construct the apparatus so as to make the external circumstances of little influence; (2) to arrange the temperature of the freezing mixture so that the convergence temperature may nearly coincide with the freezing point. The former condition may be attained by making the mass of liquid great—1,000 c.c. may be used instead of the 10 required for a molecular-weight determination—and seeing that it is well isolated, thermally, from its surroundings: an air-jacket accomplishes this. For the second condition it is necessary to watch the rate of movement of the thermometer, when the liquid is considerably above its point of temperature equilibrium; for in accordance with Newton's law of cooling, the rate at which the temperature falls will be proportional to its excess over the equilibrium temperature. Thus in an experiment by Wildermann[1], who has worked out this subject with great completeness, the thermometer, reading 0·685° to start with, fell by 30, 28, 27, 26, 25, 24, 23, 22 thousandths of a degree in successive intervals of five minutes. If these rates of fall be plotted as ordinates against the corresponding temperatures as abscissae and a line drawn through them, it will be found that no further fall of temperature will occur when the temperature of the liquid is −0·1°: this then is the convergence temperature. Usually the convergence temperature differs much more from the freezing point. So favourable a condition can only be obtained by the use of a moderate and carefully chosen freezing mixture; it should not be more than a degree or two below the freezing point to be determined. Some experimentalists have found divergences of ten per cent. from the value of the 'molecular depression' given by van 't Hoff's formula, when very dilute solutions are measured; but Nernst and Wildermann's work shows that the divergences are really too small to detect with any certainty—in other words, that the osmotic pressure may be calculated from Avogadro's law with an error less than the experimental errors of the freezing-point method.

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[1] M. Wildermann, *Phil. Mag.* (5) 44 459-86 (1897).

§ 8. Dissociation of Gases.

Measurements of the osmotic pressure, whether made directly, or by means of the change produced in the freezing or boiling point of a solution, give, in very many cases, values for the molecular weight of the dissolved substance in accordance with the commonly accepted chemical formula. Exceptions, however, occur, or especially one extensive and important group of solutions gives anomalous results, which have led to an entirely new theory on the nature of solutions. The group consists of aqueous solutions of acids, bases and salts—in a word, of all electrolytes. It is found that all solutions which conduct electricity with decomposition possess an osmotic pressure in excess of that calculated from the received molecular weight of the dissolved body. There is clearly, therefore, a connexion between the electrolytic property, and some modification of the molecular condition; and since the osmotic pressure is *increased*, the modification can, in accordance with Avogadro's law, only be a decomposition of the molecules which increases their number. The particular decomposition to which the evidence points is a dissociation into the positive and negative atoms, or atomic groups which form the electrolyte. These atoms or groups are called *ions*, the positive or *cation* being that which, in an electrolytic cell, is carried with the current, e. g. hydrogen, metals, the NH_4 group, &c.: the negative or *anion* that which moves in the opposite direction to the electric current, e. g. chlorine, the NO_3, SO_4 groups, &c.

In order to understand the view that electrolytic dissociation exists in such solutions, it is first necessary to study dissociation in general, especially in the case of gases, which, as we have seen, present a close analogy to solutions.

A dissociation, in the strict sense of the word, is a chemical reaction in which one molecule only occurs on the left side of the equation, and this decomposes into two or more. Thus

$$\begin{aligned} I_2 &= 2I, \\ N_2O_4 &= 2NO_2, \\ NH_4Cl &= NH_3 + HCl, \\ NH_4COONH_2 &= CO_2 + 2NH_3, \end{aligned}$$

are instances of dissociation, but $2HI = H_2 + I_2$ is not.

A dissociation is a reversible reaction—one, that is, that can be carried out in either sense according to circumstances, according to the pressure, temperature, and quantities of reagents. It is therefore never theoretically complete, either one way or the other, though it may for all practical purposes be so: whilst over a certain range of temperature and pressure both undissociated and dissociated molecules are present in considerable quantity together. E.g. follow out the effect of increasing temperature on the dissociation of a gas kept under constant pressure. The case of nitrogen tetroxide has been carefully studied by E. and L. Natanson and others. At low temperatures the gas is colourless, and has a density forty-six times that of hydrogen in accord with the formula N_2O_4, showing that it consists almost exclusively of the undissociated molecules: as the temperature rises it turns a red-brown colour, the colour of the dioxide, which gradually deepens till the dissociation is complete. At the same time the density diminishes, at first slowly, then faster up to a maximum, then more slowly again till it becomes sensibly twenty-three times that of hydrogen, at about 150°, the dissociation being then complete. The course of the dissociation is shown in the accompanying small figure (Fig. 8), in which abscissae represent temperatures and ordinates vapour densities: the curve for nitrogen tetroxide runs at first parallel to the axis of temperature, and after bending downwards becomes eventually again parallel to the axis, but at half the previous height. Any other physical property of the gas will be represented in a somewhat similar way. The degree of dissociation, under any condition of temperature and pressure, is the fraction of the whole number of molecules then dissociated; it may be reckoned from the vapour density. Thus if γ is the degree of dissociation and v the volume occupied by 1 gram-molecule of N_2O_4, then, since the same weight of NO_2 will occupy $2v$, we have for the actual molecular volume

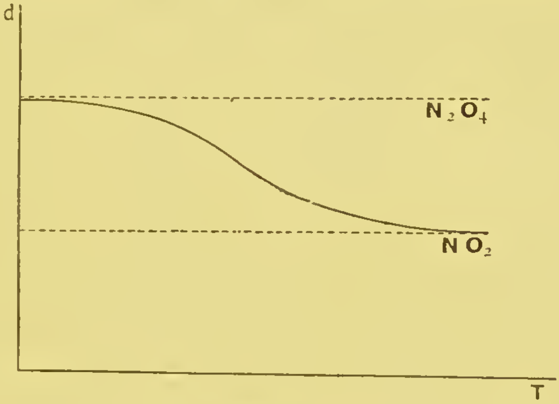

Fig. 8.

$$(1-\gamma)v+\gamma\times 2v = v(1+\gamma),$$

or $(1+\gamma)$ times as great as it would be for the undissociated gas, and the density therefore will be $1+\gamma$ times as small. For example, at 49·7° and 498 mm. the density was 31·0, referred to hydrogen at the same temperature and pressure. Hence

$$31{\cdot}0 = 46{\cdot}0 \div (1+\gamma),$$

and $\gamma = 0{\cdot}483$, showing that very nearly half the molecules are dissociated under these circumstances.

Since dissociation is accompanied by an increase of volume, the degree of dissociation is greater when the gas occupies a large volume than when it is contained in a small one; in other words, diminution of pressure is accompanied by an increase of dissociation, as is shown in the following example[1]:—

Nitrogen tetroxide at 21·5°.

Pressure.	*Sp. gr. referred to air.*	γ.	$\log K$.
59·7	2·144	0·483	1·76
117·6	2·318	·372	1·78
230·6	2·486	·279	1·79
327·1	2·589	·228	1·76
367·1	2·599	·222	1·79
492·1	2·674	·189	1·75
617·6	2·709	·174	1·76

There exists a quantitative relation between the degree of dissociation and the volume of the gas, which is a particular case of the law of mass action, a subject to be discussed later. We may content ourselves at present with stating the relation, and comparing its results with experience. The relation is this: if the reaction takes place according to the equation

$$A = \nu_B B + \nu_C C + \dots,$$

and the concentration (in gram-molecules in unit volume) of A be C_A; that of B, C_B, and so on, then

$$C_A K = C_B^{\nu_B} \times C_C^{\nu_C} \times \dots,$$

where K is a constant (the so-called 'dissociation constant'), or in words, the concentration of the undissociated molecules bears a constant ratio to the product of the concentrations of the dissociated molecules, each raised to a power equal to the number of such molecules liberated in the reaction. The simplest case is that of dissociation into two similar groups, e.g. I_2 into $2I$; then we have

$$C_{I_2} K = C_I^2,$$

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[1] Natanson, *Wied.* 24. 465; 27. 613.

so that the concentration of molecular iodine is (at a given temperature) proportional to the square of the concentration of atomic iodine. In the more complicated case of the dissociation of ammonium carbamate we have

$$C_{\mathrm{NH_4\,CO_2\,NH_2}} K = C_{\mathrm{CO_2}} \times C^2_{\mathrm{NH_3}}.$$

Reverting to the case of dissociation into two parts, if γ is the degree of dissociation, there is $1-\gamma$ undissociated molecule for γ of each product of dissociation, since the latter are necessarily produced in equal quantity; and if these quantities occur in a volume v, then by definition the concentrations are $\frac{(1-\gamma)}{v}$ and $\frac{\gamma}{v}$ respectively. The equation for the dissociation constant may be written

$$\frac{1-\gamma}{v} \times K = \frac{\gamma}{v} \times \frac{\gamma}{v} \text{ or } K = \frac{\gamma^2}{v(1-\gamma)}.$$

How closely this theory is verified by experiment is shown in the foregoing table referring to nitrogen tetroxide. The second column shows the specific gravity of the gas, at the pressure shown in the first: from it is calculated the degree of dissociation, γ, in the third column, and from that again the dissociation constant of which the logarithm occupies the last column.

The dissociation constant for gases is, of course, not independent of temperature; at low temperatures it is zero, since γ is zero, whilst at a high temperature it tends towards infinity, since γ tends towards unity.

Dissociation of a similar character occurs in some solutions which do not contain an electrolyte. Thus, for instance, when nitrogen tetroxide is dissolved in chloroform it partly dissociates into the dioxide, just as when it occurs in the gaseous form ; the 'dilution' (c.c. per gram-molecule of dissolved substance) of the solution plays the same part as the (molecular) volume of the gas, so that the more dilute the solution is made, the greater the proportion of the tetroxide dissociated. Again, acetic acid, both gaseous and in benzene solution, has a pressure corresponding to the formula $C_4H_8O_4$, and only on expansion of the gas, or dilution of the liquid, gradually breaks up into the normal molecules $C_2H_4O_2$. So also with chloral hydrate. On volatilization it breaks up partly into chloral and water, on solution in glacial acetic acid the same thing takes place; for instance, a solution containing 1·179 gms. of chloral hydrate $CCl_3CH(OH)_2$ in 100 gms. of acetic acid showed a depression of the freezing point of 0·385°. The depression calculated from the molecular weight 165 and the molecular depression for acetic acid (38·8) is $= \frac{38{\cdot}8 \times 1{\cdot}179}{165} = 0{\cdot}277°$.

The observed depression is therefore 1·38 times that due to the molecules of chloral hydrate, and it is to be concluded that 0·38 of those molecules have broken up into chloral and water. The effect of dilution is clearly shown by the measurements, as a solution four times as strong as the above indicated 0·25 dissociation, while one five times as weak indicated 0·52.

§ 9. Electrolytic Dissociation.

Such dissociation as this follows in the lines of ordinary chemical theory, and does not introduce any new groups of atoms of a character incapable of independent existence, according to accepted views; on the contrary, the products of dissociation, whether gaseous, as ammonia and hydrochloric acid from ammonium chloride, or in solution, as chloral and water from chloral hydrate, are all known independently as stable compounds; and at the same time the exceptional phenomenon of electrolytic conduction does not occur. Electrolytic dissociation, on the other hand, was quite unthought of before the theory of solutions was developed, and it is quite contrary to traditional chemical views to suppose that such a substance as sodium chloride, a typically stable compound, should dissociate on solution in water, and that free atoms of sodium and of chlorine should be capable of existence together in the same liquid. Nevertheless there is, as we shall see in the sequel, an extraordinary abundance and variety of evidence that such is the case.

In the first place, the osmotic pressure of salt solutions is greater than that calculated according to Avogadro's law, assuming the usual molecular formulae to hold for the dissolved electrolyte. We have seen that the osmotic pressure can be measured successfully either by plasmolysis or by the change of freezing and boiling points, in the case of non-electrolytes (cane-sugar, glycerine, urea, &c.) dissolved in water. There is no reason, then, to suspect the same methods when applied to electrolytes; the results are of the kind shown in the following table, which is derived from Arrhenius' measurements[1], to whom a clear formulation of the theory of electrolytic dissociation is due. The numbers show the values of van 't Hoff's factor ι, which expresses the ratio of the observed osmotic pressure to that calculated for the case of no dissociation. The first two columns show ι as found by plasmolysis and by the freezing point respectively; the third gives the values deduced from the electrolytic conductivity in a way to be explained below.

	Concentration.	ι		
		I	II	III
Cane-sugar	0·3	1·00	1·08	—
Acetic acid	0·33	—	1·04	1·01
KCl	0·14	1·81	1·93	1·86
LiCl	0·13	1·92	1·94	1·84
$MgSO_4$	0·38	1·25	1·20	1·35
CaN_2O_6	0·18	2·48	2·47	2·46
$SrCl_2$	0·18	2·69	2·52	2·51
$K_4FeC_6N_6$	0·356	3·09	—	3·07

It will be observed that the three methods give results in agreement with one another; it must be remembered that the plasmolytic method is necessarily somewhat rough, while the freezing-point method, which had not at the time been so completely worked out as at present, is somewhat uncertain when applied to very dilute solutions, as the lowering of freezing point to be observed then becomes very small; whilst it is in very dilute solutions that the phenomena of electrolytic dissociation are most marked.

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[1] *Ostw.* 1. 631.

The meaning of the quantity ι, according to the theory of Arrhenius, is this: the solution contains salt, of which a fraction, γ say, is dissociated into its ions, the remainder being in the molecular state. If there are n ions formed by the dissociation of one molecule, $n\gamma$ will actually be formed for each molecule of the salt dissolved; if to this be added the $1-\gamma$ molecules of undissociated salt still existing, we get $1+(n-1)\gamma$ free particles in the solution (molecules and ions together) in place of one. The osmotic pressure is therefore raised by the dissociation in this ratio, or

$$\iota = 1+(n-1)\gamma.$$

Now $n=2$ for acetic acid and the three salts following in the above table. ι might therefore reach a maximum $=2$ if the dissolved substances were completely dissociated; this is far from the case for acetic acid, but the neutral monobasic salts appear to be nearly in the state of complete dissociation. For calcium nitrate and strontium chloride the value of n is 3, the decomposition taking place according to the equation

$$CaN_2O_6 = Ca+NO_3+NO_3,$$

and

$$SrCl_2 = Sr+Cl+Cl.$$

Hence ι cannot exceed 3, and does, as a matter of fact, approach that value. The ferrocyanide dissociates according to the equation

$$K_4FeC_6N_6 = 4K+FeC_6N_6$$

into one negative and four positive ions, so that ι may rise as high as 5, and does in the example quoted actually exceed 3.

If this view is correct, the degree of dissociation should increase with increasing dilution (or decreasing concentration). This point has been directly proved in many cases; the following table, quoted from Wildermann[1], gives one; it refers to dichloracetic acid, which dissociates into hydrogen and the group $CHCl_2COO$. In this case then $n = 2$, and $\gamma = \iota - 1$.

Concentration.	ι *(Freezing point.)*	γ *(Freezing point.)*	γ *(Conductivity.)*
0·002599	1·966	0·966	0·956
0 005177	1·911	0·911	0·913
0·01033	1·852	0·852	0·843
0·015447	1·763	0·763	0·806
0·02048	1·717	0·717	0·731
0·02778	1·690	0·690	0·703

In the last column is inserted, for comparison, the degree of dissociation as calculated from the electrolytic conductivity. Measurements by the conductivity method are more convenient and more accurate, so that a quantitative discussion of the results may best be deferred till after that method is described.

§ 10. Laws of Electrolytic Conduction.

When a current of electricity is led through the solution of a salt (or acid, or base) the salt is decomposed, and the quantity of electricity conducted is strictly in proportion to the amount of decomposition taking place. The products of decomposition are, on the one hand, hydrogen or a metal; on the other, a halogen or acid radicle, which, however, rarely appears free, as it acts on the water of the solution, and sets free oxygen instead. The most remarkable feature of the decomposition is that the products do not appear mixed and indifferently throughout the liquid, but are guided by the current, so that the first or positive group appears only at the surface of the metallic conductor by which the current leaves the solution, and which is called the cathode, while the second or negative group appears only at the surface of the metallic conductor by which the current enters, the anode. Thus, for example, if copper sulphate solution be decomposed between platinum electrodes, the reaction is

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[1] *Ostw.* 19. 242.

$$\mathrm{CuSO_4} = \overset{+}{\mathrm{Cu}} + \overset{-}{\mathrm{SO_4}},$$

of which the latter group, reacting on water, forms sulphuric acid, which appears in the solution near the anode, and oxygen, which is given off at the anode[1].

The quantitative laws of electrolysis, which were discovered by Faraday, are as follows:—

(1) The amount of any substance liberated is proportional to the total quantity of electricity passed through the solution, independently of the rate at which it flows.

(2) The amounts of different substances liberated by the same quantity of electricity are in the ratio of their chemical equivalents.

The unit quantity of electricity is called a *Coulomb*; one coulomb flowing per second constitutes the unit current, and is called an *Ampere.*

193,080 coulombs are required to liberate two grams (one gram-molecule) of hydrogen, and therefore 16 grams of oxygen, 65 of zinc, and so on.

This result may also be expressed by means of the *electro-chemical equivalent,* which means the weight liberated by one coulomb. The electro-chemical equivalents of some of the more important substances are:—

Hydrogen . .	0·00001044
Silver	0·001118
Copper (cupric)	0·0003294
Oxygen . . .	0·00008288
Chlorine . . .	0·0003673

Electrolytic conduction unquestionably consists in a carrying of electric charges by the decomposed molecules or ions, the movement of an electric charge being, in all cases, the equivalent of a current. Thus, imagine a pair of large metallic plates connected to the poles of a battery, and a gilt pith-ball placed between them; if there is a positive charge on the pith-ball it will be repelled from the positive and attracted by the negative plate, and if free, will move accordingly, so that positive electricity will be carried from the positive to the negative side, from A to B in the accompanying figure (Fig. 9); this is equivalent to a current in the sense AB, i. e. the sense in which a current would flow if a conducting wire were laid across the gap AB. But if a negative charge exists on the pith-ball, it will be attracted by A and repelled by B, so that its motion will be in the sense BA; now a negative charge moved from B to A is equal in effect to a positive charge moved from A to B, so that in this case too a current is produced in the same sense as that in a conductor laid across AB. In an electrolyte both processes take place at the same time; a positive charge is conveyed by, say, copper ions from the anode to the cathode, while a negative charge is carried by SO_4 ions from cathode to anode, and the current actually flowing in the sum of the two; each partial current is to be estimated as the *product of the charge conveyed into the velocity of the ions conveying it.*

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[1] Or perhaps conduction takes place by means of the Cu and OH ions, the latter due to dissociation of the water itself: two OH ions, on reaching the anode, give up their charges to it and form H_2O and O.

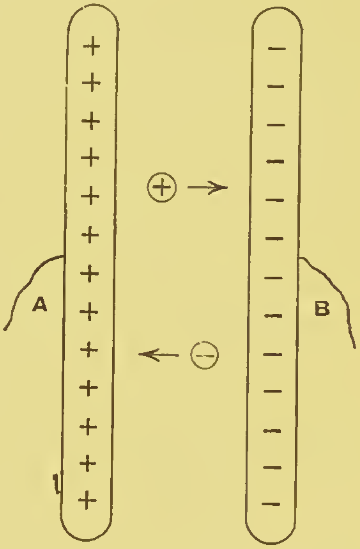

Fig. 9.

The question arises, however, whether the ions are produced by the action of the current, or whether they exist in the solution beforehand, and are only directed by the current. Everything points to the latter view; the most convincing argument being, perhaps, that derived from the quantity of energy used up in an electrolytic cell. This is expressed by the electromotive force (e. m. f. or voltage, or difference of potential) applied to the cell; the electromotive force between two points is the *amount of energy spent in conveying one unit of electricity from the one to the other*; the unit in which it is measured is called a *volt*, and means the energy in joules (10^7 ergs) spent in conveying one coulomb, or

e. m. f. in volts = energy in joules ÷ electricity in coulombs.

If the dissociation of the electrolyte were accomplished by the current, there would be a finite and considerable absorption of energy required to effect it, i. e. a finite electromotive force would be required before any decomposition occurred; but that is not the case. A finite electromotive force is, it is true, required to separate out the products of electrolysis in their usual (molecular) form; for instance, it is not possible to decompose acidulated water, and get gaseous oxygen and hydrogen out of it, without supplying the electromotive force corresponding to the absorption of energy required for the decomposition of water into oxygen and hydrogen. Nevertheless, if a smaller electromotive force than this be applied, a little current does flow, till the accumulation of gas on the electrodes is sufficient to stop it, so that free ions must exist in the solution beforehand. Again, if it be arranged that no work has to be done in separating out the products of decomposition, a current will flow indefinitely under the least e. m. f. This is the case when copper sulphate is decomposed between copper plates; the SO_4 ion acts on the anode, and dissolves copper off it in quantity just equal to that deposited on the cathode, so that, on balance, no energy is used up; accordingly it is found that the current flowing is proportional to the applied e. m. f., however small. The point is well illustrated by the phenomena of conduction in gases. Ordinary gases do not conduct electricity at all until a very high e. m. f.—some hundreds of volts—is applied to them, that amount being required for the dissociation of the gaseous molecules; but if a vacuum tube be prepared, a discharge passed through it, and a side portion be screened off from the direct electrical effects of the discharge, then dissociated gas will exist throughout the tube, and it is found that any electromotive force, however small, applied to a pair of electrodes in the side portion will produce a current. The above arguments leave it an open question whether all or a part of the electrolyte exists in the dissociated form; information on that point can be derived from a comparison of electrolytic conductivity with the effects of osmotic pressure, as we shall see below.

A remarkable confirmation of the theory of electrolytic dissociation is afforded by an experiment devised by Ostwald and Nernst[1]; they exposed an electrolyte to the action of an electrostatic force, imitating the conditions of the experiment with electrified pith-balls placed between the plates of a condenser, referred to above. They showed that electrolysis does actually take place so, the hydrogen being attracted out of an acid solution to one of the poles. The quantity of hydrogen is necessarily very minute, so in order to make it appreciable the pole on which it was to be collected consisted of a mercury surface in contact with dilute acid, in a very fine capillary tube, as in a Lippmann electrometer. The tube was 0·0037 cm. in radius, and a bubble of gas was produced in it by the electrostatic force about two diameters long, very easily visible in a microscope, and the quantity of hydrogen, though so very small, was found to be in rough quantitative agreement with that calculated from the theory.

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[1] *Ostw.* 3. 120-30 (1889).

§ 11. Mechanism of Electrolytic Conduction.

We are to imagine, then, in a solution of an electrolyte—say, for definiteness, potassium chloride—atoms of potassium, each associated with a definite positive quantity of electricity, and atoms of chlorine, each associated with a definite negative quantity, floating about freely in all directions. The positive and negative quantities must be numerically equal, otherwise, when the ions combined to form a molecule, that molecule would possess a charge, which is not the case; and the chlorine and potassium are not distinguishable as such, because, being intimately mixed, they neutralize one another's action as far as external points are concerned. When to such a system an electric force is applied, it directs the atoms, the positive one way, negative the other, and the ions appear in measurable quantity at the electrodes. The *electric force*, or electric intensity, or potential gradient, is measured by *dividing the electromotive force between two points by the distance between them*; it is therefore to be expressed in volts per cm. Thus the electric force in a copper voltameter may be measured by dividing the e. m. f. applied to the cell by the distance between the plates (supposed parallel), and it is this which regulates the rate at which electrolysis will take place.

The most important quantity to determine, so far as the theory of electrolytic dissociation is concerned, is the conductivity of an electrolyte; of this the exact definition is as follows:—

The current flowing per sq. cm. of cross section of a conductor (or *current density*) is proportional to the electric force applied (Ohm's law).

The ratio of the current density to the electric force is called the *conductivity* of the medium.

The unit of conductivity is called a mho, and is that of a medium such that an electric force of 1 volt per cm.

applied to it will produce a current density of 1 ampere per sq. cm. through it. (Frequently, however, the conductivity is not given in absolute units, but is expressed by comparison with the conductivity of mercury.)

It should be noticed that if a uniform electric force be applied to a charged body it will, in the absence of any resistance, produce a (uniformly) accelerated motion, just as the uniform force of gravity will cause a body falling freely to move downwards with uniform acceleration, i.e. get faster and faster without limit (till it meets the earth or other obstacle); the movement of a charged pith-ball placed between two condenser plates would be of this character. But if there be a frictional resistance to the movement the charged body will soon reach a limiting velocity, and cease to be accelerated. This is the case with a rain-drop, falling under the influence of gravity, on account of the resistance of the air: however far it may fall, its velocity cannot exceed a certain value, depending on the size of the drop and the density of the air; and in the same way the electrified atoms in an electrolyte, almost immediately that the force is applied to them, come to move with a limiting (average) velocity, which is quite small, on account of the frictional resistance of the water through which they have to move. It is only on this account that the current (being measured by the charge and velocity with which it is carried) is independent of the time that the electric force has acted, and that Ohm's law is true, the limiting velocity increasing in proportion to the electric force applied.

In connexion with the practical measurement of conductivities we need to use certain associated terms, viz.:

Conductance of a wire (or electrolytic cell, &c.) = conductivity of the *material* multiplied by the area of cross section, and divided by the length, or say,

$$c = \kappa \frac{A}{d}.$$

Resistivity (or specific resistance) of a *material* is the reciprocal of its conductivity.

Resistance of a wire (electrolytic cell, &c.) is the reciprocal of the conductance, and is measured in 'ohms' (reciprocal of mhos).

§ 12. Measurement of Conductivity.

For measuring conductivities an arrangement called Wheatstone's bridge is commonly adopted; it is shown diagrammatically in Fig. 10. A wire leads from the battery B to the point *a*; there the circuit divides into two branches, *abc* and *adc*, reuniting at *c*, and returning to the other pole of the battery. Two intermediate points, *b* and *d*, of the branched conductors are connected through the galvanometer G. If the resistances *ab*, *bc*, *ad*, *dc* are chosen so as to satisfy the relation

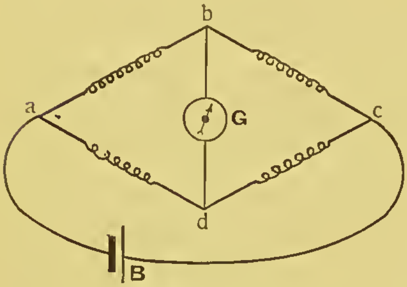

FIG. 10.

$$ab \times cd = bc \times ad,$$

then no current will flow through the galvanometer, whatever current may be taken from the battery; hence if three of the resistances are known, and the fourth is to be measured, the three can be adjusted until no current flows through the galvanometer, and the equation will then give the value of the unknown resistance. A battery and galvanometer are available, in such an arrangement, for measuring a metallic resistance, but if applied to an electrolyte the flow of current through it would generate hydrogen and oxygen on the electrodes, and consequently alter the resistance during the experiment, which accordingly fails. This 'polarization' of the electrodes by the products of electrolysis may be avoided by rapidly reversing the direction of the current, so that, at either electrode, hydrogen is produced for a fraction of a second, then oxygen for an equal time, then hydrogen again, and so on; neither gas then appears in measurable quantity. This reversal is accomplished automatically by an induction coil. But if an alternating current is used, a galvanometer will not indicate, and it must therefore be replaced by a telephone. Accordingly, the apparatus actually used for electrolytic conductivities takes the form shown in Fig. 11, and consists of the following parts:—

The source of current is a single Leclanche or dry cell, B, used to work the small induction coil I. The induction coil should be of the smallest dimensions made, and should be provided with a light rapid spring, in place of the loaded spring commonly used on large sparking coils. The object of this is to produce a clear singing tone in place of the rattle of the large induction coil, as such a tone is much more audible in a telephone: a frequency of 250 to 1000 per second in the spring gives good results—the pitch corresponding being that of a treble voice. It is desirable also to have no metal casing between the iron core and the windings, as such a casing reduces the vibrations more nearly to the simple harmonic form, which is the least audible in the telephone. Induction coils of the pattern required are now made by all the leading German scientific instrument makers.

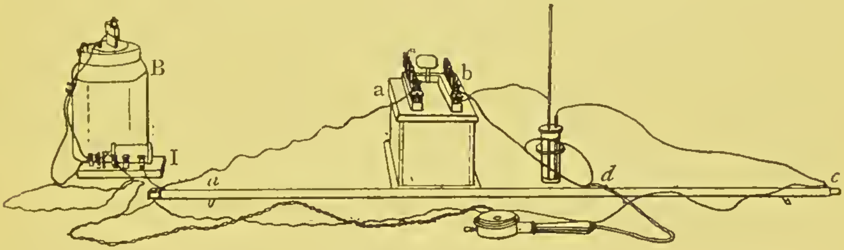

FIG. 11.

Two of the arms, *ad*, *dc*, of the Wheatstone bridge are constituted of a single uniform wire, a metre long, stretched between binding screws over a scale divided in millimetres: the point *d* is a sliding contact-maker, so that by it the wire may be divided into two parts whose lengths, and therefore resistances, are in any desired ratio. The wire should be thin, and of platinum-iridium alloy to avoid oxidation, and to be hard enough not to suffer from the action of the contact-maker. The third known arm of the bridge, *ab*, consists of a resistance box of from 10 to 10,000 ohms. The electrolytic cell may have many forms, according to the conductivity of the electrolyte to be used: but it is regularly made of glass, and provided with electrodes of platinum sealed in; and for the good working of the apparatus it is essential that the platinum should be well coated with platinum black, deposited from a solution of the chloride mixed with a little lead acetate. The electrolytic cell must be kept at a definite temperature, since the conductivity increases rapidly with rise of temperature: it may very conveniently be placed in a thermostat of Ostwald's pattern. The telephone may be any good commercial instrument. Further particulars of the apparatus may be read in Ostwald, *Handbook of Physico-Chemical Measurements*, chap. xv, or Kohlrausch, *Leitvermögen der Elektrolyte* (Leipzig, 1898).

In carrying out a measurement the solution is placed in the cell, and after it has acquired the temperature of the thermostat, an approximately equal resistance is taken out from the box, and the sliding contact-maker is moved until the sound in the telephone is least. It never disappears quite. but it should be possible to set the contact-maker to within a millimetre: the length *ad* is then read off, say *a* metres.

$$\text{Then (resistance of electrolyte)} = (\text{resistance } ab) \times \frac{1-a}{a}.$$

The conductance is the reciprocal of the resistance, or

$$= \frac{a}{(1-a) \times (\text{resistance } ab)}.$$

The electrolytic cell is not usually regular enough in shape to allow of calculating the conductivity from the conductance: this is therefore done by a comparison with the conductance of the cell when filled with a solution whose conductivity has already been measured accurately in absolute measure. A fiftieth normal solution of potassium chloride serves conveniently as a standard: containing 74·60 gms. of KCl in 50 litres it has a conductivity of 0·002397 mhos at 18° and 0·002765 at 25°. Thus, if the cell filled with a solution be found to have (at 25°) a conductance c, while filled with $\frac{1}{50}$ normal KCl it has a conductance c', then

$$c' : c :: 0{\cdot}002765 : \text{conductivity required.}$$

[Note. It should be observed that most of the German writers express conductivities of electrolytes in terms of that of mercury, or, in other words, in Siemens' units instead of mhos. The Siemens' unit is the conductance of a column of pure mercury at 0°, one square millimetre in cross section, and one metre long: it is equal to 1·0630 mhos. The specific conductivity of mercury is 10,000 times this (for conductance $= \frac{\kappa A}{d}$, and here $A = 0{\cdot}01$ sq. cm., $d = 100$ cms.) or 10,630 mhos. Now as the resistance of electrolytes is immensely greater than that of metals, a unit equal to the ten-millionth part of the conductivity of mercury, or 0·001063 mhos, is commonly adopted, so that the results may be expressed in whole numbers. Thus, e.g., when it is stated that the conductivity of normal potassium chloride solution at 18° is 91·9, this means $91{\cdot}9 \times 0{\cdot}001063$ mhos. When the conductivity is only required for estimating the degree of dissociation it is indifferent which unit is employed, as only relative measurements occur, but when calculations on ionic velocities, and so on, are introduced, there is distinct advantage in using the systematic unit, the mho. Kohlrausch and Holborn, however, in their recent monograph *Das Leitvermögen der Elektrolyte* (Leipzig, Teubner, 1898), have adopted the systematic units, and recalculated the entire mass of numerical data which had previously been published in terms of the Siemens' unit. Since, therefore, those data are now available, in the tables of the above-mentioned work, the systematic unit will be exclusively used in the present book.]

§ 13. Molecular Conductivity and Electrolytic Dissociation.

On the view that electrolytic conduction takes place entirely by means of the ions or products of dissociation present, the conductivity of a solution should be proportional to their number (at least in moderately dilute solutions), since each atom or atomic group is acted on by the electric force independently of the others. Now in an infinitely dilute solution the molecules will all be dissociated, and the conduction accomplished by a given mass of substance will be a maximum. This leads to the conception of the 'molecular conductivity,' which means the specific conductivity, κ, of the solution multiplied by its dilution V, or say

$$\Lambda_V = V\kappa.$$

If in a solution the dissolved body were already completely dissociated, then on doubling its dilution there would be only half as many ions in each cubic centimetre, the specific conductivity would be halved, and the molecular conductivity be unchanged. But if the dissociation be incomplete, the dilution will increase the degree of it; the specific conductivity will be somewhat more than half that of the stronger solution, and the molecular conductivity will be increased—tending towards the maximum value which it possesses when, in an infinitely dilute solution, the salt is entirely dissociated. Thus the ratio of the actual molecular conductivity Λ_V to the limiting value Λ_∞ expresses what fraction of the salt is dissociated when its dilution is V. Or using, as before, the symbol γ for the degree of dissociation $\gamma = \frac{\Lambda_V}{\Lambda_\infty}$, it is in this way that the results previously quoted, comparing γ as found electrically with γ found by the freezing point or osmotic pressure, were obtained.

The increase of dissociation by dilution is well shown by the following numbers for KCl at 18° (as measured by Kohlrausch):—

Dilution (c.c. per gm. molecule).	*Conductivity* (mhos).	*Molecular conductivity.*	*Degree of dissociation.*
V.	K.	$\Lambda_V = VK$.	$\frac{\Lambda_V}{\Lambda_\infty}$.
1,000	0·0982	98·2	0·75
10,000	0·01119	111·9	0·86
100,000	0·001225	122·5	0·94
1,000,000	0·0001276	127·6	0·98
10,000,000	0·00001295	129·5	0·99
∞	——	131·2	1·00

The value of Λ for infinite dilution is obtained by extrapolation from the others.

The dissociation in this case is into two ions, K and Cl; but the theoretical relation between the dilution and the degree of dissociation

$$\frac{\gamma^2}{V(1-\gamma)} = \text{constant}$$

does not hold: so that it is not possible to calculate a 'dissociation constant,' as in the case of nitrogen tetroxide quoted above. The same is true of all the neutral salts which are largely dissociated even in strong (normal or decinormal) solutions, and the reason for it is at present unknown. Weaker electrolytes, however, i. e. less dissociated, and therefore less conducting, are found to follow the theoretical relation with remarkable closeness: solutions of weak acids, in particular, have been found to follow the law of dilution, a law which is usually associated with the name of Ostwald, who has made very extensive researches on the dissociation of acids. The following numbers[1] referring to monochloracetic acid at 14·1° may serve as specimen: it should be noted that the acid is less dissociated in 2,060 litres than K Cl is in 10:—

V.	Λ_V.	γ (obs.)	γ (calc.)
20	51·6	0·166	0·163
205	132	0·423	0·43
408	170	0·547	0·543
2,060	251	0·806	0·801
4,080	274	0·881	0·88
10,100	295	0·948	0·944
20,700	300	0·963	0·971
∞	311	1·000	1·000

The numbers in the last column are calculated from the dissociation constant

$$K = \frac{\gamma^2}{V(1-\gamma)} = 1{\cdot}585 \times 10^{-6};$$

the agreement with the observed numbers is practically perfect.

The general conclusions arrived at with regard to the condition of electrolytes in aqueous solution may be briefly put as follows. Neutral salts are in general very strongly dissociated, so that in moderately dilute solution they may be treated, for many purposes, as completely dissociated; this is especially the case with regard to the salts of the alkalies: the dibasic metals are a little less dissociated, but still strongly so; and usually when the number of ions formed by dissociation is large, as in the case of potassium ferrocyanide quoted in the table p. 53, the dissociation is less complete than when only two or three ions are formed.

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[1] Van 't Hoff and Reicher, *Ostw.* 2. 781.

The acids, on the contrary, vary extremely in their degree of dissociation; they decompose into hydrogen ions, and the residue of the molecule, or 'acid radicle,' and the acid properties appear to be exclusively the effect of the free hydrogen ions, and to be proportional to their quantity: hence a strong acid means one which is largely dissociated. Thus nitric and hydrochloric acids are as strongly dissociated as the alkaline salts; sulphuric acid is nearly so; while the organic acids form an extended series with diminishing dissociation constants, the study of which has thrown much light on the connexion between their physical properties and the constitution of the molecules. The following numbers will show the great variation of the dissociation constant (K):—

	$10^5 \times K$ (at 25°).	*Degree of dissociation in $\frac{1}{1000}$ normal solution.*
Trichloracetic acid . .	121	0·999
Dichloracetic acid . .	5·1	0·981
Monochloracetic acid .	0·155	0·692
Salicylic acid	0·102	0·621
Acetic acid	0·0018	0·125

In developing the theory of electrolytic conductivity it was remarked that, though depending on the action of ions, it gave no information as to whether much or little of the electrolyte is in the ionic state. Clausius, who first clearly described the mechanism by which the conduction takes place, supposed that only an insignificant fraction was dissociated at any time; and that view was generally held until the work of Arrhenius, in tracing out the progressive dissociation by dilution, and in comparing results with those obtained by the plasmolytic and freezing-point methods, showed that in many cases nearly the whole dissolved salt exists in the form of ions.

In the case of weak electrolytes it is impossible to carry the dissociation far enough to estimate the molecular conductivity for infinite dilution, by extrapolation, as in the case of KCl. That can, however, be done indirectly. Thus, to take an example, the following numbers have been found for acetic acid at 18° :—

$V\left(\frac{\text{c.c.}}{\text{gm. mol.}}\right)$	Λ_V
10^4	4·60
10^5	14 3
10^6	41
10^7	107
[∞	352]

The conductivity of solutions much more dilute than 10,000 litres to the gram-molecule is so slight that the presence of traces of impurity in the water, and other experimental errors, forbid accurate results : the gap between $\Lambda = 107$ and $\Lambda = 352$ has to be bridged over by other means. As a matter of fact, the limiting molecular conductivity of the acid is derived from that of the sodium salt : the possibility of doing so depends on the principle, discovered by Kohlrausch, that each ion contributes independently to the conduction, the total conductivity being the sum of the parts due to positive and negative components.

§ 14. Partial Conductivity and Velocity of the Ions.

The determination of the partial conductivities of the ions depends on observations of the changes of concentration produced by electrolysis. To study this the more easily, let us take a concrete example, viz. the decomposition of silver nitrate solution between platinum electrodes. Imagine an electrolytic cell constructed of the kind shown in Fig. 12, consisting of two beakers, A and C, connected by the siphon B, which for convenience may be constructed of a glass tube with a side piece closed by rubber tubing and a spring-clip. The whole is filled with silver nitrate solution, and the platinum plates to serve as electrodes are placed, the anode in A, the cathode in C. When an experiment has been made, the siphon may be lifted out and the liquids in the beakers analyzed. Let so much current flow as will deposit one milligram equivalent, 108 mgm., of silver on the cathode, and consider the action taking place at a cross section of the siphon. Under the influence of the electric force there the charged silver atoms will be driven towards the cathode with a velocity u, while the NO_3 groups will be driven in the opposite direction with a velocity u'. Accordingly a certain quantity, let us say x milligram equivalents, of Ag will pass from the anode vessel into the cathode vessel: but as meanwhile 1 mgm. equivalent of Ag is deposited the cathode vessel will on the whole lose $1-x$ of silver. But observation shows that there is no accumulation of free ions in the liquid under any circumstances, so the cathode vessel must have lost a corresponding amount of NO_3, and that amount, $1-x$ mgm. equivalent, must have flowed through the siphon into A. The amounts of Ag and of NO_3 flowing through the siphon (in opposite directions) are therefore in the ratio of x to $1-x$, and this is the ratio of the velocities with which they move or $\frac{u}{u'} = \frac{x}{(1-x)}$.

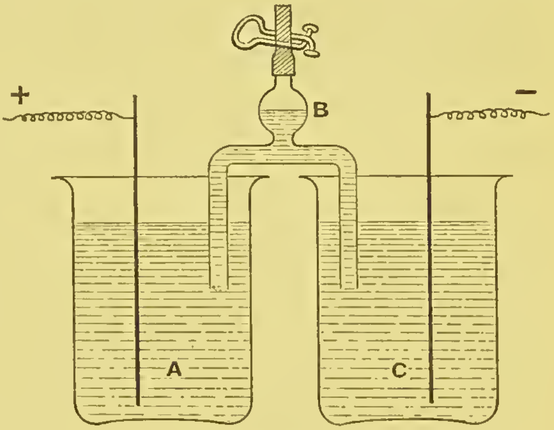

Fig. 12.

Chemical analysis will, of course, show how much $AgNO_3$ has disappeared from each of the two vessels A and C, and hence give the ratio $\frac{u}{u'}$ of the velocities of the ions. Hittorf in this way determined the relative velocities for a large number of positive and negative ions. Thus in the case of silver nitrate $x = 0{\cdot}472$, showing that the negative NO_3 ions move rather faster through the liquid than the positive Ag.

But each positive and negative ion carries the same quantity of electricity with it (else when they united to form a molecule that molecule would not be electrically neutral); hence the strength of current due to each ion must be proportional to its velocity, in other words the conductivity of the electrolyte may be divided into two parts, due to the two constituents separately, and these two parts will be in the ratio of x to $1-x$.

Now in the case of strongly dissociated electrolytes the measurements of Kohlrausch and others give the value of Λ_∞, i. e. the molecular conductivity when completely dissociated. This for silver nitrate solution is 116·5; combining with this the observation of the relative velocities, it follows that the partial (or ionic) conductivity of the Ag is $0{\cdot}472 \times 116{\cdot}5 = 55{\cdot}7$, while that of the NO_3 is 60·8. The number thus obtained for the partial conductivity of an ion is (allowing for experimental errors) the same, from whichever of its compounds it is determined: that fact constitutes the proof of the assumption with which we started—that the partial conductivities are independent of one another.

The following are some of the most important results arrived at: the values for H and OH being derived from the conductivity of strong acids and bases.

Partial (or ionic) conductivities at 18°.

K	65·3	Cl	65·9
NH_4	64·2	Br	66·9
Na	44·4	I	66·7
Li	35·5	NO_3	60·8
Hg	55·7	ClO_3	56·2
H	318	$C_2H_3O_2$	33·7
		OH	174

One of the chief uses of this table of partial conductivities is to determine the limiting molecular conductivity, and hence the degree of dissociation of substances which it is impracticable to dissociate completely. Thus in the case of acetic acid, quoted above, the conduction due to the $C_2H_3O_2$ ion may be found from measurements on the sodium salt, which like all the sodium salts is almost completely dissociated at moderate dilutions. Being found 33 7, it follows that Λ_∞ for the acid is $33{\cdot}7 + 318 = 351{\cdot}7$.

Ostwald gives certain rules with regard to the more complex organic acids, which show the regularity with which the ionic velocity, in these cases, falls off with increase of molecular weight. His values at 25° reduced to systematic units are:—

Acids with	12	atoms	Λ_∞	= 380
,,	14	,,	,,	= 379
,,	15	,,	,,	= 378
,,	18	,,	,,	= 376
,,	22	,,	,,	= 374
,,	25	,,	,,	= 373
,,	30	,,	,,	= 372

So far, we have only considered the relative velocities of the ions; it is not difficult, however, to determine their absolute amounts. Let u and u' be the velocities (in cm. per second) with which the ions are moving across a certain section of the liquid, and f be the electric force, or gradient of potential there (in volts per cm.); V the dilution (cc. per gm. mol.). Then across one square cm. there flows in a second the cation contained in a space whose length is u cms. and cross section 1 sq. cm., i. e. u c.c.s. The mass of cation contained in this volume is (provided the electrolyte be completely dissociated) $\frac{u}{V}$ gm. equivalents. But one gm. equivalent carries 96,540 coulombs, therefore the current carried by the cation (per sq. cm. cross section) is

$$96{,}540 \, \frac{u}{V} \text{ amperes.}$$

A similar expression holds for the anion, and as the total current is the sum of the two, we have

$$\text{current density} = \frac{96{,}540\,(u + u')}{V} \text{ amperes.}$$

Now the conductivity is the ratio of the current density to the electric force producing it, or

$$\text{conductivity } \kappa = \frac{96,540\,(u+u')}{Vf};$$

whence

$$u+u' = \frac{\kappa Vf}{96,540} = \frac{\Lambda_\infty f}{96,540},$$

Λ_∞ being written since the argument requires complete dissociation. But Λ_∞ may be divided into its component parts, proportional to u and u'. For hydrogen, e. g., the partial conductivity at 18° is 318 mhos.
Hence we may write

$$u = 318f \div 96,540 = 0{\cdot}00329f.$$

Putting this result into words we may say, for example, suppose the electromotive force of a Daniell cell (1·1 volt) applied to electrolyze a dilute solution of hydrochloric acid, between electrodes placed at a distance of 1·1 cms. Then the potential gradient in the electrolyte is 1 volt per cm., and accordingly the hydrogen of the acid will move in the direction from negative to positive plate with a speed of 0·00329 cms. per sec., or one centimetre in about five minutes. The atoms will of course, as a matter of fact, be moving about in all directions with a speed that is enormously greater; i. e. will share the undirected motions common to all the atoms and molecules present, which constitute its heat energy. These motions, however, would lead the hydrogen nowhere, since they are distributed with complete indifference in all directions. What the electric force does, is to superimpose on that a steady drift in one direction, which will gradually lead all the hydrogen atoms to the cathode, where they will appear in the molecular form.

CHAPTER II

PHYSICAL CONSTANTS IN RELATION TO CHEMICAL CONSTITUTION

Systematic study of the physical properties of a large number of definite chemical compounds has led to certain generalizations as to the way in which the physical constants depend on the arrangement of the atoms in the molecule. Knowledge of this subject is still in a very rudimentary state, the laws or generalizations arrived at being purely empirical, but it cannot be doubted that eventually, when the constitution of the molecule of any compound is sufficiently well known, it will be possible to calculate all the physical properties of that compound from the properties of its elements; just as it is now possible to calculate the weight of the molecules from the weights of its component atoms. At present all that is possible is to give an account of the chief physical constants to be measured, the apparatus used for measuring, and the leading empirical results obtained.

As far as the determination of physical constants is concerned, the material to be experimented on may be divided into three classes—(i) fluids (liquids and gases), (ii) ordinary—isotropic—solids, (iii) crystals. The first and third of these classes are well suited to the purpose, provided sufficient care be taken to obtain the materials in a state of chemical purity; ordinary solids, such as the metals, on the other hand, are very difficult subjects of investigation, because in general their properties—e. g.

density, elasticity, electric conductivity—depend on the mechanical treatment that the solid has undergone. So that even if the preliminary difficulty of obtaining a chemically pure material be overcome—which is not easy, because frequently a small trace of impurity produces a disproportionately large effect on the physical properties—the material will show varying properties according as it is cast, rolled, wire-drawn, annealed, &c., i. e. according to the previous history of the specimen used; whereas fluids, if of identical chemical composition, are always of identical physical properties, or to use a mathematical phrase, the various physical constants of a fluid are functions of the state of the fluid at the moment, while in solids that is not in general the case. Hence very few data of value have been arrived at with regard to the physical properties of solids.

§ 1. Density of Fluids.

The most important constant to measure in a fluid is its density (or specific volume) under varying conditions of temperature and pressure.

[If p be the pressure on the fluid,
T its absolute temperature,
v its specific volume,
there exists a relation

$$f(p, v, T) = 0,$$

which is called the *characteristic equation* of the fluid. The various measurements described below give the means of determining the form and constants of this equation, over various portions of the entire range of temperature and pressure. The simplest instance of a characteristic equation is that of a perfect gas,

$$pv = RT.$$

Another of importance is van der Waals' equation, to which we shall have to return in detail below.]

The problem of determining the density under all possible circumstances presents itself under different forms according to the conditions of pressure and temperature: the most important cases are—

(i) absolute measurement of density under ordinary conditions;
(ii) measurement of the coefficient of expansion under constant pressure;
(iii) measurement of compressibility at constant temperature;
(iv) determination of the critical constants.

Apparatus for measuring the density of gases and vapours has been described in chap. i. Liquids can be measured in any form of specific gravity bottle or pyknometer, of which the best pattern is the Sprengel tube, as modified by Ostwald. This consists of a wide tube *c* with a capacity of, conveniently, 5 or 10 c.c., terminating in the tubes *a* and *b* of about one millimetre bore: *a* is drawn out slightly at the end, *b* bears a mark near the middle of the horizontal portion. The tube is filled by dipping *b* under the surface of the liquid in a small dish, and sucking at the end *a* through an india-rubber tube. When full, the rubber tube is slipped off, and the pyknometer placed upright in a water bath; in two or three minutes it acquires the temperature of the bath, and the quantity of liquid in it is then adjusted to the mark on *b*. The capillary effect of the narrow end of *a* keeps *a* full, so that if a piece of filter paper be held against *a*, liquid will

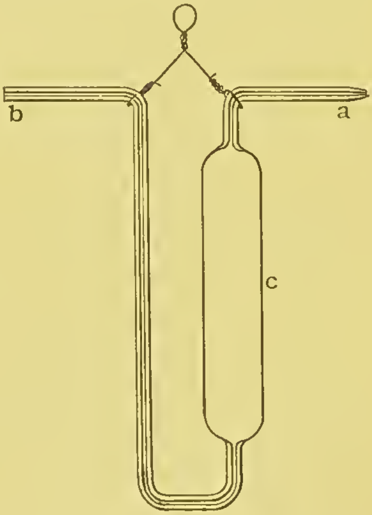

FIG. 13.

be withdrawn from *b*. If there is too little liquid, a drop on the end of a glass rod is held against the end of *a* and liquid will flow into *b*. The tube is then taken out of the bath, wiped with a linen or silk cloth, and weighed. Evaporation does not take place rapidly from the small exposed surfaces in a Sprengel pyknometer, so that it may be used for water and aqueous solutions without any trouble. For more volatile liquids, glass caps ground to fit the ends serve to prevent evaporation.

The conditions of pressure and temperature under which the weighing is made are sufficiently definite: for the fluctuations of atmospheric pressure do not produce a variation of more than $\frac{1}{200000}$ part in the volume, while the temperature is that of the water bath, and may conveniently be read to $\frac{1}{100}^\circ$, which corresponds, for an ordinary liquid, to a variation of about $\frac{1}{100000}$ in the volume. To make a set of comparable measurements, it is desirable to use a thermostat, so as to keep the pyknometer, during filling, always at the same temperature. An account of suitable thermostats is given in Ostwald's *Handbook of Physico-Chemical Measurements*, chap. v.

Two corrections have to be applied to the density as measured: (*a*) for displacement of air, (*b*) for the density of water at the temperature of observation. The density of air may be taken as 0·0012 gms. per c.c. under ordinary conditions of weighing: hence for every cubic centimetre of liquid in the pyknometer 1·2 mgms. of air are displaced; but from that must be deducted the displacement by the weights; if the latter are of brass this amounts to 0·15 mgms. of air per gm. of weight. Accordingly the true weight of water is 1·00105 times the apparent weight, while to get the true weight of the experimental liquid we must add 1·2 mgms. for each c.c. and deduct 0·15 mgms. for each gram. If then three weighings be made with the pyknometer, (i) dry, (ii) full of water, (iii) full of the liquid to be measured, calling the difference of (i) and (ii) W_0, and the difference between (i) and (iii) W, we have

true weight of water $= W_0 \times 1{\cdot}00105$,
true weight of experimental liquid

$$= W + 0{\cdot}0012\,W_0 - 0{\cdot}00015\,W,$$

and the specific gravity referred to water at the temperature of the experiment is

$$D = \frac{W + 0{\cdot}0012\,W_0 - 0{\cdot}00015\,W}{W_0 \times 1{\cdot}00105}.$$

This must be multiplied by the density of water at t° to give the actual density of the other liquid. The density of water is given in the following table[1]: the temperature is measured on the normal hydrogen scale.

Temperature.	*Density.*	*Specific volume.*
0°	0·9998679	1·0001321
3·98	1	1
10	0·9997272	1·0002728
15	0·9991263	1·0008745
20	0·9982298	1·0017733
25	0·9970714	1·0029372
30	0·9956732	1·0033456
35	0·9940576	1·0059779
40	0·9922417	1·0078190

§ 2. Thermal Expansion of Fluids.

The absolute density or specific volume of a liquid having been determined at one temperature by the pyknometer, the change of density with temperature may most conveniently be found by a dilatometer such as that shown in Fig. 14. It consists of a bulb of 5 to 10 c.c. capacity, provided with two capillary tubes: of these, one is merely for the purpose of convenient filling, the other plays the same part as the tube of a thermometer. The end of *b* is immersed in the liquid to be measured, and by sucking at *a* the dilatometer is filled as far as the lowest mark on a. The end of b is then closed, best by a small glass plate, held in place by a screw, and provided with a scrap of sheet rubber to make the joint tight. The tube is then immersed in a water bath, and heated till the liquid reaches the various marks on the tube in turn. In order to use a fine tube for a and yet not too long, several small bulbs may be blown on it. The volume of the main bulb and of the various divisions of a is determined by calibration with mercury. A more perfect closure of the end of b may be obtained by drawing out, and after filling fusing in the flame: but this alters slightly the volume of the dilatometer at each experiment.

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[1] Thiessen, Scheel, and Diesselhorst, *Wied.* 60. 340–9 (97).

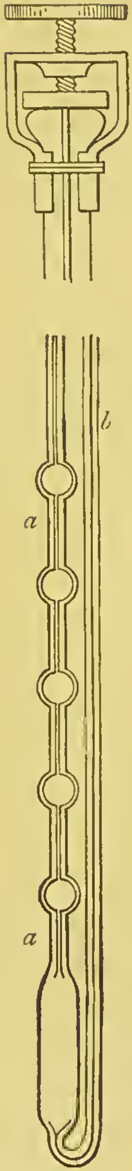

Fig. 14.

If v_0 be the volume of the bulb and so much of the tube as is occupied by liquid when at the freezing point, v_t the volume occupied at t°, then the apparent *mean coefficient of expansion* between 0° and t° is $\frac{v_t - v_0}{t v_0}$.

The coefficient is, however, actually greater than this by the coefficient of expansion of glass, which may be taken as 0·000025. If the coefficient of expansion is the same at all temperatures, the volume at t° may be written

$$v_t = v_0 (1 + at):$$

more generally an equation in three terms,

$$v_t = v_0 (1 + at + bt^2),$$

is required to express the experimental results with sufficient accuracy. [In the latter case, the true coefficient of expansion at t_0 is

$$\frac{1}{v_0} \frac{dv}{dt} = a + 2bt.]$$

§ 3. Vapour Pressure and Critical Point.

While observations with the pyknometer and dilatometer are within the ordinary practice of a laboratory, and may be made with ease on any liquid that is to be studied, measurements of compressibility of liquids are difficult, and require more elaborate apparatus. The same is true with regard to the compression of gases, when measurements are to be made with sufficient accuracy to show the deviations from Boyle's law. We will therefore only make use of certain results obtained, and refer for details to the text-books of physics, and especially to the classical papers of Amagat[1].

When a gas is compressed, the temperature being kept constant, it may condense to a liquid, or it may become continuously denser and denser but without showing any sudden transition. Which of the two will happen depends on the temperature of the gas; below a certain point called the *critical temperature*, liquefaction occurs on the application of sufficient pressure; two layers of fluid—the denser, liquid, and the lighter vapour—then exist in equilibrium; if the volume occupied by the fluid be then reduced further, that will only result in the condensation of more of the vapour, without rise of pressure, so long as any vapour is left. The pressure existing when the two layers of fluid are in equilibrium is known as the maximum or *saturation pressure*. If the temperature be above the critical point no such phenomena are observed, the fluid being homogeneous however strongly compressed.

The critical point may be observed by forcing a sufficient quantity of gas into a strong glass tube closed by a mercury column. The tube is surrounded by a jacket of liquid or vapour to maintain a constant temperature, and pressure applied by means of the mercury; the temperature of the bath is then adjusted so that compression can be carried out without the formation of two layers, but on cooling very slightly, condensation may be observed when the pressure is given the right value. In this way the critical point for carbon dioxide, which is about 31°, may easily be observed, and the corresponding pressure, the limit to the saturation pressure as the temperature reaches the critical value, is found to be 73 atmos. If the substance experimented on is liquid at ordinary temperatures the same process may be adopted, and the filling of the tube needs no special appliances. A few gases, e.g. hydrogen, oxygen, carbon monoxide, have critical points much below the atmospheric temperature, and accordingly require special cooling baths, but otherwise the experimentation is similar. In any case, the critical pressure may be read off a gauge attached to the compression apparatus, and the critical volume, i. e. the specific volume of the fluid under critical temperature and pressure, may be estimated, at least roughly, if the compression tube be calibrated; for details, see S. Young[1]. When, on account of high pressure or chemical activity, glass tubes are not available for the experiment, a method due to Cailletet and Colardeau[2], and used by them for water, may be adopted. A steel tube of ample strength is taken, and an amount of the fluid placed in it, shut off by

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[1] E. H. Amagat, *Ann. Chim. Phys.* (4) 29. (5) 8. 11. 19. 22. 28. 29.

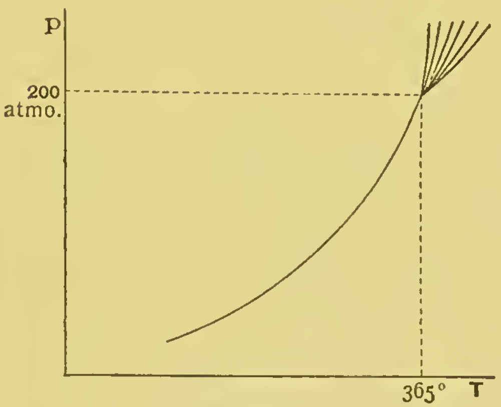

Fig. 15.

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[1] S. Young, *Phil. Mag.* (5) 33. 153-85 (1892).

[2] Cailletet and Colardeau. *Ann. Chim. Phys.* (6) 25. 519-34 (1892).

mercury, such that on heating to the critical point it will neither altogether evaporate nor fill the tube with liquid; so long as the critical temperature is not reached, there will be a definite saturation pressure corresponding to each temperature, however much fluid be used, provided the above condition is satisfied. If the results of the experiments are shown graphically, a single *vapour pressure curve* (Fig. 15) will be obtained. Beyond the critical point, however, the pressure in the tube will be greater, the more fluid it contains; and by making a series of measurements with different quantities of fluid, a sheaf of curves will be obtained, branching out from the critical point, which is thus defined.

§ 4. Theoretical Relations at the Critical Point: Law of Correspondence.

Numerous attempts have been made to express the results of measurement on the relation of volume to pressure and temperature by a single equation which shall be applicable to both liquid and gaseous states. The most important of these attempts is that of van der Waals. Other equations than his have been found which express the experimental results more closely, but they are more complicated, and contain a greater number of arbitrary constants, and so are less intelligible theoretically; we shall therefore only refer to van der Waals' equation[1].

The characteristic equation to a perfect gas, $p = \frac{RT}{v}$, when applied to an actual substance, is found to depart from the truth chiefly in the two following ways: (i) it implies that when the pressure on the gas is indefinitely increased the volume would be indefinitely diminished, whereas experiment shows that the volume tends to a finite limiting value, below which it cannot be reduced by any pressure, however great; (ii) when the volume of the fluid is small there is an appreciable surface tension, which, acting like an elastic skin over the fluid, balances a part of the internal pressure due to the movement of the molecules, leaving only the remainder to be equated to the applied external pressure. The phenomenon of surface tension is well known in liquids, and it may reasonably be taken to depend on the closeness of the molecules of a fluid and the consequent forces of attraction between them, and accordingly should be shown by a highly compressed gas as well as by a liquid. Van der Waals took the pressure thus produced to be inversely proportional to the square of the specific volume of the fluid, getting thus a term $\frac{a}{v^2}$ to be added on to the external pressure in order to arrive at the pressure actually obtaining in the interior of the liquid: a being a constant for each fluid. Hence there is a pressure $p + \frac{a}{v^2}$ to produce compression, and van der Waals assumed that this is inversely proportional to the excess of the volume over the limiting volume b, or

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[1] Van der Waals, *On the Continuity of the Liquid and Gaseous States of Matter.* English translation, 164 pp. Taylor & Francis, London.

$$p + \frac{a}{v^2} = \frac{RT}{v - b}.$$

This equation, which may be regarded as a first approximation to the truth, brings out, *inter alia*, the phenomenon of the critical point: remembering that the critical point is the limit at which the two states, liquid and saturated vapour in equilibrium, pass over into a single state, gas, it is possible to calculate the critical temperature (T_C), pressure (p_C), and volume (v_C), the results being

$$T_C = \frac{8a}{27bR},$$

$$p_C = \frac{a}{27b^2},$$

$$v_C = 3b.$$

[Van der Waals' equation is a cubic in v, having in general three different roots; the critical point is that for which the three roots are equal, i. e. the three values of v corresponding to a given pressure and temperature become identical.]

It follows that if the constants in van der Waals' equation be obtained by measurements taken over any range of pressure and volume, the critical constants may be calculated from them. Or conversely, if it is more convenient to measure the critical point experimentally, the equation may be written down by that means, and so the volume corresponding to any other pressure and temperature be calculated. The most important of the three relations just mentioned is the third, which states that the specific volume in the critical state is three times the limiting volume under indefinitely great pressure. Since in a liquid under ordinary conditions the volume is nearly as small as the limiting volume, the critical volume is approximately three times that in the liquid state.

Van der Waals' equation leads to a very important conclusion if the volume, pressure, and temperature be expressed as fractions of their critical values. So expressed they are called the *reduced* volume, say $\omega = \frac{v}{v_C}$, pressure $\pi = \frac{p}{p_C}$, and temperature $\tau = \frac{T}{T_C}$. Substituting ω, π, and τ for v, p, and T in the original equation, we get

$$\left(\pi + \frac{3}{\omega^2}\right)(3\omega - 1) = 8\tau,$$

an equation containing no arbitrary constant. That is to say, the relation between the *reduced* volume, pressure, and temperature is the same for all substances. This result may be otherwise expressed as follows:—if two fluids be taken under conditions of pressure and temperature, which are the same fractions of their respective critical pressures and temperatures, then their volumes will be the same fraction of their respective critical volumes; such conditions are known as *corresponding* pressures and temperatures, and the *law* is sometimes called that *of corresponding states.*

It should be carefully noted that though van der Waals' equation leads to the law of corresponding states, that law, if true, does not necessarily imply the truth of van der Waals' equation. The relations between volume, pressure, and temperature may conveniently be represented by means of a diagram in which p and v are taken as ordinate and abscissa, and lines are drawn showing the relations at successive constant temperatures (*isothermal lines*). If such diagrams be drawn for two substances, and then the scales of one of them be altered so as to make the two critical points coincide, the law of correspondence implies that the two sets of isothermals will coincide throughout, whether they have the particular shape calculated from van der Waals' equation or not. Amagat made comparisons of the kind by means of an optical apparatus which formed a magnified or reduced image of one diagram on the paper bearing the other, so that a glance was sufficient to tell whether the two coincided or not.

The most complete tests of the law of corresponding states are contained in the papers of Amagat[1], who made measurements on six gases and twelve liquids, in apparatus of special construction, capable of standing 1,000 atmos. pressure at a temperature of over 200° and 3,000 atmos. at ordinary temperatures; and of Young[2], whose measurements, made on some twelve substances, all liquid under ordinary circumstances, reached to more than 400° in temperature, but in pressure only to some 75 atmos.; a range, however, sufficient to include the critical points of the liquids chosen. Young chose fluorbenzene as a typical organic liquid, for a standard of comparison, and prepared tables showing, at successive corresponding temperatures, the ratio of the saturation pressure of each liquid to that of fluorbenzene; if the law of correspondence be true, the ratio of the vapour pressures will be constant. Similarly other tables showed the specific volumes of the liquid and saturated vapour of each fluid by comparison with those of fluorbenzene, and again the numbers are constant or variable according as the law of correspondence holds or not. We have not space for anything more than brief extracts from Young's results, of which the first may be the table of critical constants, following.

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[1] *Ann. Chim. Phys.* (6) 29. 68–136, 505–74 (93).

[2] S. Young, *Phil. Mag.* (5) 33. 153–85 (92).

Substance.	*Formula.*	*Mol. wt.*	T_C (abs.).	p_C (mm. of Hg.).	v_C (c.c. per gm.).
Fluorbenzene . . .	C_6H_5F	95·8	559·55	33,912	2·822
Chlorobenzene . . .	C_6H_5Cl	112·2	633·	33,912	2·731
Bromobenzene . . .	C_6H_5Br	156·6	670·	33,912	2·059
Iodobenzene	C_6H_5I	203·4	721·	33·912	1·713
Benzene	C_6H_6	77·84	561·5	36,395	3·293
Carbon tetrachloride .	$C\,Cl_4$	153·45	556·15	34,180	1·799
Tin tetrachloride . .	$Sn\,Cl_4$	259·3	591·7	28,080	1·347
Ethyl ether	$(C_2H_5)_2O$	73·84	467·4	27,060	3·801
Methyl alcohol . . .	CH_3OH	31·93	513·0	59,760	3·697
Ethyl alcohol . . .	C_2H_5OH	45·90	516·1	47,850	3·636
Propyl alcohol . . .	C_3H_7OH	59·87	536·7	38,120	3·634
Acetic acid	CH_3COOH	59·86	594·6	43,400	2·846

From these numbers corresponding temperatures may be reckoned, e. g. 410·4° abs. is, for fluorbenzene, 0·7335 of the critical temperature; to this corresponds, for ethyl alcohol, 378·85°, since

$$\tau = \frac{410{\cdot}4}{559{\cdot}55} = \frac{378{\cdot}55}{516{\cdot}1} = 0{\cdot}7335.$$

Experiment shows that at 410·4° fluorbenzene has a vapour pressure of 3,000 mm., while at 378·55° alcohol has 2,042 mm. These two numbers are, however, not the same fraction of the critical pressures of the two liquids: the reduced pressures are

$$\text{for fluorbenzene } \pi = \frac{3{,}000}{33{,}912} = 0{\cdot}0885,$$

$$\text{for alcohol } \pi = \frac{2{,}042}{47{,}850} = 0{\cdot}0427.$$

Accordingly the law of correspondence is far from being verified in the case of alcohol. On the other hand, it is very approximately true for substances of similar chemical constitution; this appears in the following table for chlorobenzene:—

τ.	π (fluorbenzene.)	*Ratio.*
0·486	0·0006	0·998
0·639	0·0223	1·005
0·733	0·0885	0·993
0·822	0·2360	1·000
0 928	0·5900	1·007
1·000	1·0000	1·000

The third column shows the ratio between the vapour pressure of chlorobenzene and that of fluorbenzene. It does not differ from unity by more than can be accounted for by experimental errors.

The chief conclusions that Young arrives at are as follows:—the law of correspondence is true very approximately, if not exactly, for the group of halogen derivatives of benzene; it is a rough approximation to the truth as regards comparisons between fluorbenzene and carbon tetrachloride, stannic chloride, and ether; it is not at all true for comparisons between fluorbenzene and the alcohols or acetic acid, except as regards the molecular volume of the liquid at corresponding temperatures or pressures. But the three alcohols, methyl, ethyl, and propyl, show about as much correspondence amongst themselves as in the group CCl_4, $Sn\,Cl_4$, $(C_2H_5)_2O$. Further, when only an approximate correspondence exists, it is closest, in the case of the volume either of liquid or saturated vapour, at corresponding pressures.

Certain empirical relations have been discovered in the course of measurements on the critical state, of which one of the most important was stated by Cailletet and Mathias, under the name of the *law of rectilinear diameter.* It is found that the sum of the densities of the saturated vapour and liquid at any temperature is a linear function of the temperature: this rule extends up to the critical point where the two densities become identical. Accordingly, if a curve be drawn showing the relation between density D and temperature T (Fig. 16), it will be approximately parabolic in shape, the branch CL showing the density of the liquid under its own vapour pressure, and CV that of the saturated vapour. If the mean between the two be found, at various temperatures, points will be obtained, the locus of which is a diameter of the curve LCV according to the definitions of geometry. That diameter appears to be very exactly a straight line, except in the case of water, and one or two more abnormal liquids. As this law appears to hold, for most liquids, quite up to the critical point, the critical density can be found by marking off points on the diameter and producing that line upwards till it reaches the critical temperature. This is preferable to direct measurement of the critical volume, for, as appears from the curve, a very small change in pressure produces a very great change of volume in the neighbourhood of the critical point, so that

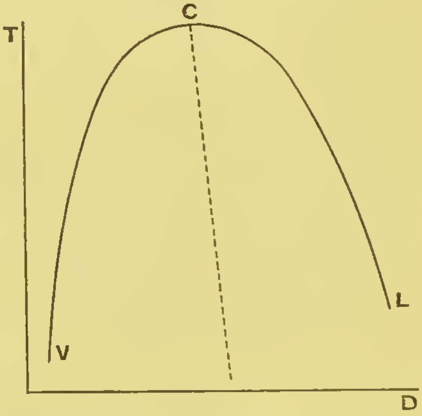

Fig. 16.

the volume can only be determined roughly; the numbers given by Amagat and others for the critical volume are found by means of the law of rectilinear diameter.

Results of observations on the behaviour of fluids under varying pressure and temperature may be conveniently expressed by the ratio of the actual to the theoretical density; meaning by the latter term, the density the fluid would possess under the given pressure and temperature if it were a perfect gas. Now the molecular volume of a perfect gas is $= \frac{RT}{p}$, so that if v be the actual molecular volume of a fluid at pressure p and temperature T, the ratio $v : \frac{RT}{p}$ is that between the actual and theoretical volumes, or $\frac{RT}{p} : v$ between the corresponding densities. S. Young finds that at the critical point the latter ratio is very close to 3·8 for benzene and its halogen derivatives $C\,Cl_4$, $Sn\,Cl_4$, and ether; while the anomalous liquids examined by him give

	$\frac{RT}{p} : v$.
Methyl alcohol	4·54
Ethyl alcohol	4·04
Propyl alcohol	4·04
Acetic acid	5·03

To these may be added, from other sources,

Water	3·10	(Battelli)
Carbon dioxide	3·62	(Amagat)

It may be noted that, according to van der Waals' equation, we should have

$$\frac{RT_C}{p_C} = \frac{8a}{27b} \times \frac{27b^2}{a} = 8b,$$

while

$$v_C = 3b.$$

So that the ratio of the actual to theoretical density at the critical point would be 8 : 3. It is found to be greater than this in all the above cases, and van der Waals' equation is only to be regarded as a rough approximation to the truth.

§ 5. Atomic Volume.

While the general relations between volume pressure and temperature have so far led to hardly any knowledge of chemical constitution beyond the distinction between normal and abnormal liquids, certain regularities have been observed on comparing the volumes of many different liquids under more restricted, but still comparable, circumstances. Kopp first employed the conception of the *molecular volume*, and in order to get comparable results measured it always at the *boiling point* of the liquid *under atmospheric pressure.* In doing so he practically adopted temperatures such as have since been defined as 'corresponding,' for the boiling point of a liquid differs but little from two-thirds of its critical temperature. Under this condition Kopp endeavoured to show that the molecular volume may be regarded as the sum of terms contributed by the various atoms in the molecule, and which he accordingly called the *atomic volumes.*

The atomic volumes of the elements entering into the composition of organic substances are given by Kopp as follows:—

Carbon	11·0
Oxygen	7·8
(Carbonyl oxygen) .	12·2
Hydrogen	5·5
Chlorine	22·8
Bromine	27·8
Iodine	37·5
Sulphur	22·6

These numbers are obtained by comparing the molecular volumes of a large number of compounds, and are such as come nearest to satisfying the conditions thus given, but they must not be looked upon as exact. The molecular volume is not, in fact, an *additive* property; i. e. it cannot be expressed as the sum of parts each of which refers to one of the atoms only; rather, for an exact treatment of the subject, the constitution of the molecule would need to be considered; in one instance, indeed, constitution is taken into account in the above list of values. The influence of an oxygen atom on the molecular volume of the compound varies too much to be expressed even roughly by one number, but oxygen compounds may be divided into two classes, with an approximately constant atomic volume for each; when the oxygen atom has both its valencies saturated by the same carbon atom, forming the carbonyl group (= C = O), its volume in the compound is 12·2, in other cases it is 7·8.

By means of the above table the molecular volume of a liquid may be calculated with accuracy, usually of two or three per cent. As an example, acetone, $CH_3 . CO . CH_3$, gives

3 Carbon atoms	33·0
6 Hydrogen atoms . . .	33·0
1 Carbonyl oxygen atom .	12·2
	78·2

for the theoretical molecular volume.

Its molecular weight is 58·05, and its density at its boiling point (55·5°) = 0·749, hence the actual molecular volume is 58·05 ÷ 0·749 = 77·5.

It has been found more difficult to express the behaviour of nitrogen by means of an assumed atomic volume, than the other elements, as its influence varies largely according to its position in the molecule. For further details with regard to molecular volumes we must refer to Ostwald's *Lehrbuch d. Allg. Chemie* (vol. 1), where the subject is treated at length; many rules applicable to particular groups of bodies have been worked out, but no generalizations of importance arrived at so far.

According to J. Traube[1], the molecular volume is more exactly expressed by adding to the sum of the atomic volumes a certain constant which he calls the co-volume.

§ 6. Refractive Index.

The refraction of light by transparent liquids furnishes a set of physical constants which may be conveniently and accurately measured, and which are found to possess regularities similar to those of the molecular volume; much study has been devoted to the problem of calculating the constants of refraction from the composition and constitution of the compounds, and we shall give some of the leading results below. When light passes from one medium into another it is found, usually, that the incident ray, the refracted ray, and the normal to the surface between the media, are in one plane. (The exceptions are in certain cases of refraction by crystals, with which we are not at present concerned.) The angles made by the incident and refracted rays, respectively with the normal, are called the angles of incidence and of refraction. If these be called ϕ_1, ϕ_2, it is found (still with the exception of certain crystals) that

$$\mu_1 \sin \phi_1 = \mu_2 \sin \phi_2,$$

where μ_1, μ_2 are constants depending on the nature of the media, and are called the refractive indices. It is immaterial which of the two angles is regarded as the angle of incidence, for if a ray of light will pass along a certain path in one sense, it will pass along the same path in the opposite sense, so that the incident and refracted rays are really interchangeable. Numerical values for the refractive indices are obtained by choosing that of air, or of vacuum, as unity. Accordingly, if one of the two media, say the first, be air, as commonly happens, the above equation reduces to

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[1] J. Traube, numerous papers in the *Ber. d. Deutsch. Ch. Ges.*, 1891, and onwards.

$$\sin \phi_1 = \mu \sin \phi_2,$$

and measurement of the angles yields the value of μ, the refractive index of the second medium. Air and vacuum do not differ much in refractive index from one another, but in exact work it is necessary to define precisely the standard adopted, which is most frequently air, free from water vapour, at 15° C. and 760 mm. pressure. Such air has a refractive index (for sodium light) of 1·000277 referred to a vacuum.

The refractive index of a liquid may best be measured by means of a spectrometer. A spectrometer consists essentially of an illuminated slit placed at the principal focus of a lens (the collimating lens) arranged so as to throw a beam of parallel light on one face of a prism of the substance to be measured; the beam is deviated on passing through the prism, and on emergence received by a telescope focussed for parallel rays. The path of the light is shown in Fig. 17. ABC is a plan of the prism, the refraction depending on the angle A between the two working faces BA and CA. A ray follows the path LMOP, making at the first surface the angle of incidence LMN, and

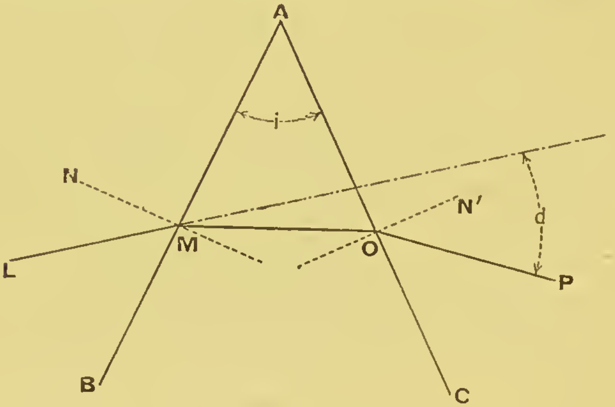

Fig. 17.

at the second the angle of emergence N′OP. In general it would be necessary to measure these two angles as well as the angle at A in order to find the refractive index of the prism; if, however, the prism is put symmetrically with regard to the collimator and telescope, so that LMN=N′OP, the number of angular measurements required is reduced by one. It is then only necessary to observe the angle of deviation (which is then a minimum), i.e. the angle between LM and OP, or between the axis of the collimator and the axis of the telescope. Then it may be shown that if

i = angle of the prism at A,
d = angle of deviation,

$$\mu = \frac{\sin \frac{i+d}{2}}{\sin \frac{i}{2}}.$$

To measure a glass or a crystal, a solid prism is cut from the specimen and its angles determined. For a liquid, a hollow prism of glass is employed; this is usually made by drilling a hole 1 to 2 cm. in diameter horizontally through the prism between the faces AB, AC, and closing the ends of it by carefully ground glass plates. A hole in the top of the prism allows of pouring in the liquid and inserting a thermometer; the effective angle of the prism of liquid is then the angle between the faces AB, AC, as the glass plates, if ground truly parallel-sided, are without influence on the result. For details of construction and use of the spectrometer reference must be made to the handbooks of laboratory practice; it belongs, however, to the most accurate of physical instruments; an accuracy of 1 in 10,000 is easily obtained by it, and with a first-rate instrument 1 in 1,000,000 may be approached. In order to obtain such results, however, a corresponding degree of accuracy must be attained in measuring the temperature of the substance forming the prism. The temperature coefficients of the refractive indices of solids are mostly small, and may be neglected except when the highest precision is aimed at; that is not the case with liquids, except perhaps water and aqueous solutions. The following short table will give a notion of the magnitude of the correction involved:—

	Refractive indices for sodium light	
	at 18°.	*decrease per* 1°.
Ethyl alcohol . . .	1·3624	0·00040
Benzene	1·5024	64
Carbon disulphide .	1·6294	79
Water	1·3331	08

Accordingly, the organic liquids mentioned may be measured to 1 in 10,000 if their temperature be observed to about $\frac{1}{5}$ degree, but to get results correct to six places of decimals would need the practically unattainable condition of a temperature constant and known to $\frac{1}{500}$ degree.

The spectrometer, however, is a somewhat tedious and inconvenient instrument to use. For rapid measurement of the refractive index of a liquid several instruments have been devised, of which probably the best is that of Pulfrich. The most essential parts of this are shown in Fig. 18. A right-angled prism stands with its faces vertical and horizontal, and bears on the upper face a short glass tube some 15 mm. in diameter. The tube is attached with cement, and serves to contain the liquid to be measured, of which one or two grams is sufficient; it is closed at

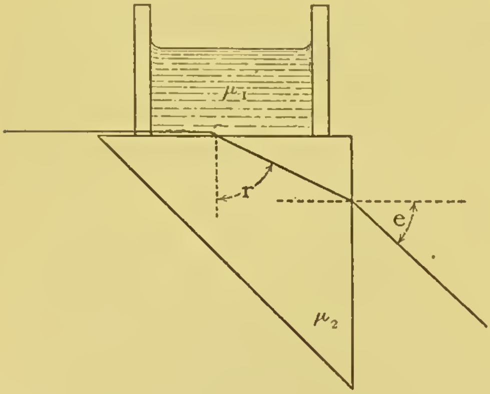

Fig. 18.

the top by a cork, through which a thermometer passes. A sodium flame at a distance of about one metre is focussed by a lens so as to form an image edgeways on the surface between the liquid and the glass of the prism; the beam is refracted downwards into the prism, making an angle with the normal to the prism face which cannot be greater than r, the critical angle for grazing incidence. r is given by the condition that

$$\mu_1 \sin 90^\circ = \mu_2 \sin r\,;$$

whence $\sin r = \frac{\mu_1}{\mu_2}$, where $\mu_1 =$ refractive index of the liquid, $\mu_2 =$ refractive index of the glass. Thus the limiting ray makes an angle of incidence on the vertical face $i = 90^\circ - r$, and emerges into the air making the angle e, given by

$$\mu_2 \sin (90^\circ - r) = \sin e.$$

Hence

$$\mu_1 = \mu_2 \sin r = \mu_2 \sqrt{1 - \sin^2 i} = \sqrt{\mu^2_2 - \sin^2 e}.$$

The angle e is observed by means of a telescope moving round a graduated vertical circle; if the telescope be turned so as to make the required angle with the horizontal, the lower half of its field of view will come within the refracted beam, while the upper half is dark; the cross wires of the telescope are set on the boundary between the two. The setting may be accomplished with an accuracy of about half a minute of arc, corresponding to about 0·00005 in the refractive index. The instrument is adapted also for use with 'hydrogen light,' i. e. the glow from a vacuum tube containing hydrogen, and which consists of three rays, in the red, blue, and violet respectively, and it may be used with a heating jacket round the prism for measurements at temperatures above the atmospheric.

The results of measurements of refractive index may be more conveniently expressed by a function of the refractive index and the density than by the index alone. The refractive index, in fact, for a given substance depends on the pressure, temperature, and state of aggregation; being greater, the more dense the substance. The connexion is most clearly seen in the case of gases, which require special methods of measurement, for there the indices are only slightly greater than unity; the excess $\mu-1$, reckoned from vacuum, may be regarded as due to the gaseous matter present, and it is found, in fact, that when the concentration (density) of the gaseous matter is altered by pressure or temperature, the difference of refractive index from vacuum is altered in the same ratio; i.e. if d be the density, or v the specific volume,

$$(\mu-1)v = \frac{\mu-1}{d} = \text{constant for any one gas.}$$

This quantity, known as the specific refracting power, has been used in the case of liquids by Gladstone and Dale, and by Landolt, to express the relations of refraction to chemical composition. It is, in fact, nearly independent of changes in density of liquids brought about by temperature, but it does not so satisfactorily express the effect of a change from the liquid to the gaseous state. Thus, for water (using sodium light), it is found that

		$(\mu-1)v$
Liquid at	0°	0·3338
	10°	0·3338
	100°	0·3323
Steam		0·3101

Another formula, proposed independently by Lorentz of Leyden and by Lorenz of Copenhagen, is

$$\frac{\mu^2-1}{\mu^2+2}v.$$

For gases, this quantity is almost exactly proportional to the other, but for substances whose refractive index is appreciably different from unity it gives different results. It is found to possess a value more nearly independent of temperature and state of aggregation than the other; thus for water,

Liquid at	0°	0·2061
	10°	0·2061
	100°	0·2061
Steam		0·2068

It is, therefore, well adapted to show the influence of chemical composition on refraction. If the value of the specific refracting power as expressed by either of these two formulae be multiplied by the molecular weight, the result may be called the molecular refracting power; and it is found possible to express it as the sum of atomic refractions with about the same degree of accuracy as in the corresponding case of molecular volumes.

The refractive index of all substances varies according to the wave-length of the light used, being, with the exception of a few anomalous cases, greater for short wave-lengths (blue end of the spectrum) than for long (red end). Definite points in the spectrum are distinguished by the presence of bright or dark lines due to the action of certain elements, bright when the emission spectrum of a gas is observed, dark against a bright background in the spectrum of the sun. The most prominent of these lines have received the letters of the alphabet as names, those most employed in measurements of refractive index being—

	Wave length (in air).
C (hydrogen: red)	6·563 $\times 10^{-5}$ cm.
D_1 (sodium: yellow)	5·896
D_2 (sodium: yellow)	5·890
F (hydrogen: blue)	4·8615

The two D rays are very close together, so that in a spectroscope of small dispersion they appear as one, and are often treated as such.

A large mass of observations has been accumulated by Brühl, Conrady, Kannonikoff, and others, from which certain values for the atomic refractions of the elements have been derived, expressing most nearly the experimental results. The influence of constitution is not to be neglected, however; if a fixed value be given to the effect of each atom, only a rough approximation is obtained. To get the theory into closer accord with facts, terms must be introduced into the molecular refraction depending on the mutual connexion of the atoms. Conversely, when this has been done, the rules arrived at throw light on the constitution of any new compound whose refractive index is measured, and may therefore become a valuable aid in studying the constitution of carbon and nitrogen compounds. Brühl, especially, has made considerable advances in this direction, but his work is too long to reproduce here[1].

The principal atomic refractions, calculated from the formula of Lorenz and Lorentz, are given in the following table:—

	C.	*D.*	*F.*	*F—C.*	
Carbon	2·365	2·501	2·404	0·039	at 20° C.
Hydrogen	1·103	1·051	1·139	0·036	
Chlorine	6·014	5·998	6·190	0·176	
Bromine	8.863	8·927	9·211	0·348	
Iodine	13·808	14·120	14 582	0 744	
Oxygen (hydroxyl)	1.506	1·521	1·525	0·019	
Oxygen (ether)	1·655	1·683	1·667	0·012	
Oxygen (carbonyl)	2·328	2·287	2 414	0·086	
Nitrogen (attached to *C* only)	2·76	—	2·95	0·19	
Additional for double *C* bond	1.836	1·707	2·056	0·23	
Additional for triple *C* bond	2·22	—	2·41	0·19	

The values for the *D* ray are from Conrady's measurements, and do not agree very well with the others, which are due to Brühl.

These numbers may be used in the same way as the atomic volumes. Thus, e.g., benzene has at 20° the density 0·8799 and refractive index 1·4967 for the *C* ray; hence, the molecular weight being 78·05, the molecular refraction is

$$\frac{1{\cdot}4967^2-1}{1{\cdot}4967^2+2} \times \frac{78{\cdot}05}{0{\cdot}8799} = 25{\cdot}94.$$

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[1] J. W. Brühl, *Ostw.* 16. 193, 226, 497, 512 (1895); 22. 373 (1897); 25. 577; 26. 47 (1898).

The value calculated from Brühl's numbers is

6 carbon atoms at 2·365 = 14·190
6 hydrogen atoms at 1·103 = 6·618
3 double bonds at 1·836 = 5·508
26·32

the error amounting to a little over one per cent.

In mixtures the specific refraction may be calculated from those of the components, in proportion to the masses present. Thus, if a mixture be made up of m_1 grams of a substance A and m_2 grams of B, its refractive index μ is given by the equation

$$\frac{m_1}{m_1+m_2}(\mu_1-1)\,v_1+\frac{m_2}{m_1+m_2}(\mu_2-1)\,v_2=(\mu-1)\,v,$$

where μ_1, μ_2 are the refractive indices of the components, v_1, v_2 their specific volumes, and v the specific volume of the mixture; or else by

$$\frac{m_1}{m_1+m_2}\,\frac{\mu^2_1-1}{\mu^2_1+2}\,v_1+\frac{m_2}{m_1+m_2}\cdot\frac{\mu^2_2-1}{\mu^2_2+2}\,v_2=\frac{\mu^2-1}{\mu^2+2}\,v.$$

The latter appears to be slightly the more exact of the two. The rule is of importance because it may be applied to find the specific refraction of one component when the other is known; thus, if a solid be dissolved in a liquid, its specific refraction may be calculated from the density and refractive index of the solution, together with the corresponding constants for the solvent alone.

The change of refractive index with change of wave length in the light used is called *dispersion*. It may, e. g., be measured by the difference between the refractive indices of the same substance for the C and F rays: and may be referred to *atomic dispersion* in a manner similar to the refraction. The differences between the atomic refractions for the C and F rays, constituting the atomic dispersion over that range, are given in the last column of the preceding table.

The dispersion of ordinary media may be fairly represented by an equation of the form (due to Cauchy)

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4},$$

where λ is the wave length of the light. If the wave length be very great the later terms of the expression become zero, and the refractive index is $= A$. The refractive index for long wave length is closely connected with another quantity—the dielectric constant.

§ 7. Dielectric Constant.

When a battery is connected to an electric circuit but the circuit is not 'closed,' i. e. a gap of non-conducting material is left in it, a certain quantity of electricity flows from the battery and accumulates on the two insulated ends of the circuit, until their electric potentials become the same as those of the poles of the battery with which they are connected. The quantity flowing is, in an ordinary circuit, almost immeasurably small, but if the metallic surfaces opposed to one another, and constituting the ends of the circuit, are enlarged, the quantity may be greatly increased. The arrangement of metallic surfaces is then called a condenser: thus a condenser may conveniently be made of two parallel brass plates, separated by a thin layer of air, or of two sheets of tinfoil separated by a sheet of glass or of paraffined paper. The action of such a condenser may most conveniently be expressed by means of its *capacity*, which is defined as the ratio of the quantity of electricity flowing on to the plates to the electromotive force of the battery which causes it to flow. The unit of capacity corresponding to the practical units of quantity and e. m. f. is called the *farad*; hence

$$\text{capacity in farads} = \frac{\text{quantity in coulombs}}{\text{e. m. f. in volts.}}\cdot$$

The farad is, however, an enormously large capacity: so that the millionth part of it, called one microfarad, is used in practice.

It is found that the capacity of a condenser depends on the nature of the insulating substance, or *dielectric* between its plates: the capacity of an air condenser is increased when the air is replaced by another dielectric, in a fixed ratio; the ratio to air (or more strictly to a vacuum) is called the *dielectric constant* of the medium. Now according to the view that light is an electro-magnetic disturbance, it may be shown (following Maxwell) that

$$\mu^2 = K,$$

where K is the dielectric constant; only as K is always measured by means of stationary charges or by oscillations which are very slow compared with those of light, and consequently of very much greater wave length, in order to test the theory K must be compared with the refractive index for indefinitely long wave length, or

$$A^2 = K.$$

This relation appears to be strictly true for gases—which are absolute non-conductors. E. g. Boltzmann found for air at 0° and atmospheric pressure (referred to vacuum),

$$K = 1{\cdot}000590,$$

while $A^2 = 1{\cdot}000576$. . . . . (Benoît)

It is nearly true for a certain number of liquids; thus toluene at 20° gives

$$K = 2{\cdot}227,$$
$$A^2 = 2{\cdot}176,$$

but it is not even approximately true for liquids that are not very good insulators. Water, and even alcohol, belong to this class, for though pure water is very much less conducting than solutions of salts and acids, it is millions of times more so than the hydrocarbons. Accordingly, while μ^2 is less than 2 for both water and alcohol, the dielectric constants of those liquids are,

Alcohol (at 14°)	25·8
Water (about)	80·

The expression for the specific refraction given by Lorenz and Lorentz is, however, based upon the above consequence of the electro-magnetic theory of light. It was shown by Clausius that if a dielectric be regarded as composed of a number of conducting spherical atoms immersed in a non-conducting medium (the ether), then the increase of capacity of a condenser due to the dielectric could be accounted for, and the dielectric constant calculated in terms of the space actually occupied by the atoms. Calling the latter quantity u (fraction of the whole volume),

$$K = \frac{1+2u}{1-u},$$

whence

$$u = \frac{K-1}{K+2},$$

and if

$$K = \mu^2,$$

$$u = \frac{\mu^2-1}{\mu^2+2},$$

consequently the volume (per gram) actually occupied by the atoms is obtained by multiplying this expression by the specific volume v,

$$= \frac{\mu^2-1}{\mu^2+2}\,v,$$

and a constant is thus arrived at necessarily independent of pressure, temperature, or state of aggregation.

Apart, however, from any theory as to its connexion with the phenomena of light, the dielectric constant is coming to possess considerable importance for chemistry. It is observed that the substances possessing the highest dielectric constants are those which when used as solvents are the most effective in promoting reaction between substances dissolved in them, and especially in causing electrolytic dissociation, and the acid and alkaline reactivity accompanying dissociation. Thus water, methyl alcohol, formic acid, and liquid ammonia possess the highest known dielectric constants, and they all produce marked electrolytic dissociation.

The method now usually adopted to measure the dielectric constant of a liquid is modified from the Wheatstone bridge method for resistances[1]; the arrangement of apparatus is shown in Fig. 19. The 'quadrilateral' of the bridge is formed of two resistances, R_1, R_2, each of about 40,000 ohms, and two condensers, C_1, C_2. The latter are of adjustable capacity, being made of a pair of metal plates with a sliding glass plate between; when the glass plate is pushed in to replace the air between the metal surfaces the capacity is increased, and by a known quantity proportional to the movement of the plate: the latter is regulated by a micrometer screw, so that the change in capacity of either condenser is readily calculated. An induction coil, I, similar to that used in measurements of electrolytic resistance, supplies current to the system, and a telephone, T, is placed between the junctions of the condensers to their respective resistances. When the ratio of the capacities is inversely as that of the resistances ($C_1 : C_2 = R_2 : R_1$), the conjugate condition is attained, i. e. no current will occur in the

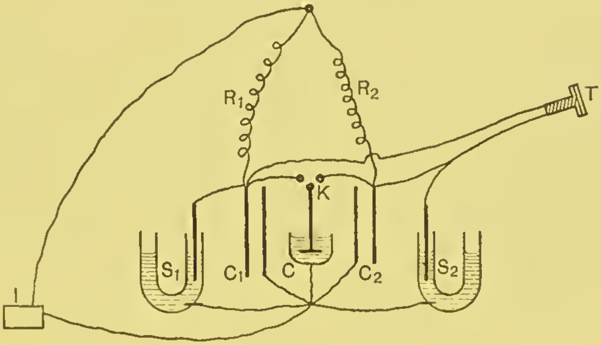

FIG. 19.

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[1] Nernst, *Ostw.* 14. 622-63 (1894).

telephone circuit. In practice the resistances, R_1, R_2, are made equal, and therefore the minimum sound in the telephone indicates that $C_1 = C_2$. C is a trough provided with electrodes; it is filled with the liquid to be measured, and constitutes a liquid condenser; by means of the key K it is placed in parallel, first with C_1 and then with C_2. Suppose C_1 C_2 adjusted to equality and C then placed in parallel with C_1, the capacity of that branch is increased, and the micrometer of C_2 must be turned till equilibrium is restored; the distance through which the micrometer is turned then measures the capacity that has been added to C, i. e. the capacity of the liquid condenser. The minimum in the telephone is, however, usually somewhat indefinite, owing to slight conduction through the liquid. To remedy this two very high adjustable liquid resistances, S_3, S_4, are put in parallel with the condensers and adjusted so that the total conductivity is the same on both sides of the quadrilateral; the indication of the telephone then becomes clear.

§ 8. Viscosity.

The coefficient of viscosity and the surface-tension of liquids have also been measured, with a view to determining the influence of the atoms and of their arrangement on the physical properties of the molecule, especially in organic compounds. To measure the viscosity the method invariably adopted is to observe the rate of flow of the liquid through a capillary tube.

It may be shown that if a liquid be forced through a capillary tube by means of a constant pressure, the coefficient of viscosity η (as defined in the introduction) is determined by

$$\eta = \frac{\pi r^4 tp}{8lv},$$

where $\pi = 3{\cdot}1416$, $r =$ radius of the tube, $l =$ length of tube, t is the time taken for the volume v to flow, and p the pressure applied. If in this equation the length and radius are expressed in cm., the volume in c.c., the time in sec., and the pressure in dynes per sq. cm., the coefficient will be obtained in C. G. S. measure. Practically the pressure is applied by means of a 'head' of the liquid itself, or of water or mercury; the head of liquid must then be multiplied by its density and by the acceleration of gravity to give the pressure in the required unit.

For absolute measurements all the quantities in the above equation must be observed; but usually the viscosity of some well-known liquid, such as water, may be taken as a standard, and that of any other liquid determined by observing the comparative rates of flow through the same capillary tube. If the pressure in a pair of comparative observations be produced by the liquids themselves, and the head be the same in the two cases, the comparison may be conveniently made by observing the time of flow of the same volume of each liquid, and then it follows from the above equation that

$$\frac{\eta_1}{\eta_2} = \frac{t_1 D_1}{t_2 D_2},$$

where D stands for the density, and the suffixes 1, 2 refer to the first and second liquids respectively.

A very convenient apparatus for comparative measurements has been described by Ostwald, and is shown in Fig. 20. It is constructed entirely of glass tubing: $b\,d$ is the capillary, terminated above by a bulb k of three or four c.c. capacity. A pair of marks c and d are made on the capillary itself, and the neck just above the bulb where the tube is narrowest. The wide end $e\,f$ is bent up so that the whole apparatus may be arranged in a water bath, with the working parts well immersed. This is important, because the viscosity changes very rapidly with the temperature (often two per cent. per degree), so that unless the temperature of the liquid in the capillary is accurately known, measurements are useless. To use the apparatus a *fixed volume* of liquid is introduced at *f* by means of a pipette, and *a* being attached to a water pump, the liquid is sucked up till it rises above the mark *c*; it is then allowed to flow down again, and the times at which the level falls to *c* and to *d* observed. If the same volume of each liquid be used, the difference of level between the two tubes (i. e. the head of liquid) at the moment of passing either mark is necessarily the same in the two cases, and although the head varies a little during the course of the experiment, the preceding equation will hold good. Only a small amount of liquid is needed, and it may obviously be used again and again; it is necessary to use some care in avoiding dust in the liquid, as that would partly choke the capillary, and so lead to error; but the precaution is the less difficult the wider the capillary, and as the pressure used in Ostwald's apparatus is small the capillary need not be very fine: a diameter of half a millimetre usually suffices to make the time of flow reasonably long.

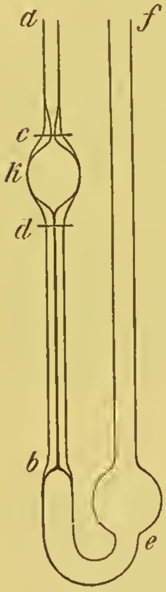

FIG. 20.

When it is desired to measure the coefficient in absolute units, it is necessary to determine the length and diameter of the capillary tube used. To determine the diameter is not easy, since it is a small quantity, and as it occurs in the equation, raised to the fourth power, a small error in measuring it produces a much larger error in the result: the diameter is usually found from the weight of mercury required to fill the tube; and the variation of diameter must be found by calibrating, as in a thermometer.

Thorpe and Rodger[1] have measured the coefficient of viscosity of a large number of organic liquids over a range of temperature extending from the boiling point of each liquid down to 0° C. The apparatus, which was more elaborate than that of Ostwald, and admitted of determining η in absolute units, was nevertheless constructed entirely of glass, and arranged so that it could be immersed in a bath of water or glycerine.

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[1] *Phil. Trans.*, 1894, or more briefly *Proc. Roy. Soc.* 55. 148.

Thorpe adopts Slotte's formula to express the influence of temperature, viz. :—

$$\eta = \frac{c}{(1+bt)^n},$$

in which b, c, n are constants, and t the temperature centigrade. In the case of most liquids (not water or alcohol) this may be simplified to

$$\eta = \frac{c}{1+\beta t+\gamma t^2}.$$

The chief conclusions arrived at were that (1) in homologous series of compounds the viscosity increases with the molecular weight; (2) that it is greater for normal than for the corresponding iso-compounds; (3) that it is generally less for the more symmetrical of a pair of metameric substances than for the other; (4) it is changed by a definite amount by substitution, e.g. of a halogen for hydrogen, but not by the same amount on substitution of a second halogen atom. The lowest members of each series are abnormal in their behaviour; and the rules given do not apply to the liquids regarded as 'associated' (e.g. alcohols, glycols, water); these associated liquids possess unusually large temperature coefficients of viscosity. The authors tabulate (1) the coefficient of viscosity (η) for the various liquids; (2) the product $\eta \times v^{\frac{2}{3}}$, where v is the molecular volume: this product is called the *molecular viscosity*, being proportional to the force required to drive a molecule with unit velocity through the liquid; (3) the product $\eta \times v$, called the *molecular viscosity work*, from being proportional to the work required to move a molecule with unit velocity through a distance equal to the mean distance between the molecules of the liquid.

These three quantities may be fairly expressed as sums of terms relating to the component atoms, with others referring to the more important features of configuration in the molecule; but the comparison must be made at the proper temperatures. The boiling point of each liquid (as used by Kopp) will serve: Thorpe and Rodger give the following values for the molecular viscosity (in dynes × 10^4) at the boiling point under atmospheric pressure:—

Hydrogen	80	
Carbon	98	
Hydroxyl oxygen .	196	$(-C-O-H)$
Ether oxygen . . .	35	$(-C-O-C-)$
Carbonyl oxygen .	248	$(-C=O)$
Ether sulphur . .	155	$(-C-S-C-)$
Chlorine	284	
Bromine	420	(in monobromides)
Bromine	479	(in dibromides)
Iodine	520	
Iso-grouping . . .	15	
Double bond . . .	113	
Ring	610	

The values calculated from these data are usually within five per cent. of the truth. The fact that boiling points are not strictly corresponding temperatures may be expected to produce a greater error here than in the molecular volumes, since the variation with temperature is greater; but an attempt to use 'corresponding temperatures,' as defined by van der Waals, did not lead to any better results, on account of the uncertainty of the critical data.

A third method of comparison was to choose such temperatures as made the slope of the viscosity temperature curve the same in all cases, i.e. the temperature variation of the viscosity $\left(\frac{d\eta}{dt}\right)$ constant for all the liquids. The viscosity at temperatures so chosen may be expressed by means of atomic constants somewhat better than the same quantity at the boiling point. Outstanding discrepancies are attributed to either (1) influence of the constitution of the molecule other than in the half-dozen important cases tabulated above; or (2) molecular aggregation.

§ 9. Surface Tension: Molecular Aggregation of Liquids.

The most definite evidence of molecular aggregation is, however, that afforded by measurements of surface tension. An extensive research on this point has been made by Ramsay and Shields[1], containing measurements of the surface tension of certain liquids from atmospheric temperature up to their critical points, and deductions which allow of calculating the actual molecular weight of the liquids. We will begin by describing the simpler of two forms of apparatus used by the authors, and which will serve as a good example of the well-known capillary-tube method of measuring surface tension. A (Fig. 21) is a glass tube of about 1 cm. diameter to contain the liquid: inside it is placed the capillary, G, sealed on to a wider tube, D, which serves to keep the capillary upright and in the centre of A, while allowing it to move freely up and down. At F a small hole is blown, which puts the liquid inside the capillary into communication with that outside: and inside D is a spiral of iron wire. H H is a magnet which by its attraction on the iron wire serves to draw the capillary down to any desired point; by its means the level of liquid in the capillary is adjusted to one or two mm. from the top of G. The adjustment is important, because the theory of the capillary-tube method assumes that the radius of the tube is measured at the point to which the liquid rises: the diameter can conveniently be measured at the end with a microscope,

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[1] *Phil. Trans.* 184. 647.

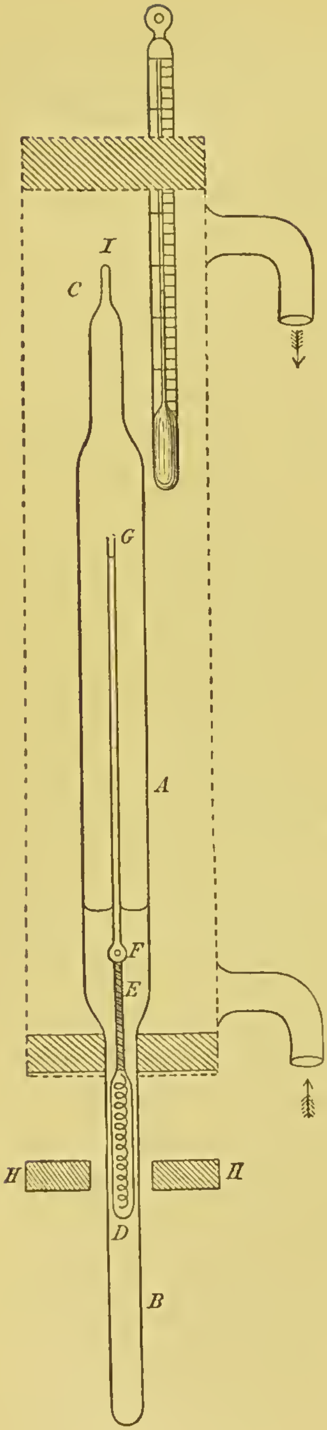


Fig. 21.

and if the liquid meniscus be always brought very close to the end, the radius so measured may be taken as correct, independently of any slight variation in bore of the tube. 0·2 to 0·3 mm. is a convenient bore for most liquids. The liquid is placed in the tube A, well boiled to drive out air, and the end I sealed. The apparatus is then fitted into a small water or vapour jacket C to ensure a known temperature, and the difference of level between the inner and outer menisci measured with a travelling microscope. A small correction must be made for the fact that the cross section of A is not very great, and consequently the liquid stands a little higher in it than it would in a vessel of indefinitely great area. The surface tension is given by

$$\tau = \tfrac{1}{2} ghr(D-d),$$

where D is the density of the liquid, and d (in this case) the density of the saturated vapour; the latter becomes considerable as the critical point is neared, but at low temperatures may be neglected.

The apparatus above described was only used at moderate temperatures, a more elaborate form serving for the experiments above 100°. But an even simpler arrangement serves when the surface tension is measured between the liquid and air, as is commonly the case: the tubes may then be left open.

The laws which the surface tension of liquids follows are best expressed by the quantity known as the molecular surface energy. The surface energy per square cm. is numerically equal to the surface tension per linear cm., and is therefore expressed by τ; but if it be referred to an area containing a constant number of molecules more intelligible results are obtained. If V be the molecular volume of the liquid (c.c. per gm. mol.) the cube root of $V = V^{\frac{1}{3}}$ will be proportional to the average distance between the molecules in the liquid, and hence the square of that quantity ($V^{\frac{2}{3}}$) will express an area on which a constant number of molecules is distributed. The product $\tau V^{\frac{2}{3}}$ is therefore the surface energy calculated for a fixed number of molecules, or, briefly, the molecular surface energy. Ramsay and Shields find that the molecular surface energy is a linear function of the temperature over a very wide range. At the critical temperature (t_C) liquid and vapour become identical, so that the surface between them disappears, and the surface tension, of course, becomes zero. Accordingly the expression

$$\tau V^{\frac{2}{3}} = K(t_C - t)$$

is nearly true, the surface energy at any temperature (t) being proportional to the number of degrees that temperature lies below the critical point. More precisely it is found that the temperature should be reckoned from about six degrees below the critical point, and that in the neighbourhood of the critical point itself the relation is more complicated, but to determine the constant K for any liquid it is only necessary to measure the molecular surface energy at two temperatures and divide the difference by the interval of temperature,

$$\left[\text{or} \quad K = \frac{d}{dt}(\tau V^{\frac{2}{3}})\right].$$

It is found that K has approximately the same value for all liquids which show no signs of molecular aggregation. The value is about 2·12, but it fluctuates about five per cent. on both sides of that average. The agreement is, however, sufficiently good to show that there is a definite physical meaning attributable to the constant; the meaning becomes clearest when the equation is compared with the characteristic equation of a gas, viz. $pv = RT$. K plays in the former equation a part analogous to that of R in the latter, as becomes apparent in the parallel statements:

'In all normal gases, at temperatures equally removed from the absolute zero, the product of the pressure into the molecular volume is the same.'

'In all normal liquids, at temperatures equally removed from their critical points, the product of the surface tension into the "molecular area" is the same.'

The latter statement is, however, considerably less exact than the former.

If, however, the molecular weight of a substance in the liquid state be greater than that expressed by its usual formula (based on observations of the vapour), then the molecular volume will be greater in the same proportion; if the rule with regard to molecule surface energy still remains true, it is clear that the value of K in the above equation (V being calculated from the usual chemical formula) will be too small. As a matter of fact, Ramsay and Shields found the following values for certain abnormal liquids over the range 16° to 46°:—

	K.	x.
Methyl alcohol	0·933	3·43
Ethyl alcohol	1·083	2·74
Propyl alcohol	1·234	2·25
Glycol alcohol	1·036	2·92
Formic acid	0·902	3·61
Acetic acid	0·900	3·62
Propionic acid	1·446	1·77

These are all liquids which from their other physical properties give indications of the existence of complex molecular aggregates; if then we assume that K has always the value 2·12, and modify the preceding equation by writing xV for the molecular volume instead of V, the experiments will allow of calculating x. We have approximately

$$\tau (xV)^{\frac{2}{3}} = (t_C - t) \times 2{\cdot}12$$

[more correctly the differential equation

$$\frac{d}{dt}\{\tau (xV)^{\frac{2}{3}}\} = 2{\cdot}12].$$

x will then express how many times the molecular weight (or volume), as calculated from the usual chemical formula, must be increased to give the true molecular weight (or volume); it may be called the *factor of association.* The values of x given in the above table are calculated in that manner: rise of temperature regularly produces a decrease in the value of x, indicating that the molecular aggregates tend to break up on heating. This is shown by the values for water:—

Temperature.	*Factor of association.*	*Temperature.*	*Factor of association.*
5°	3·81	85°	2·79
25°	3 44	105°	2·61
45°	3·13	125°	2·47
65°	2·96		

Accordingly the average weight of a molecular group in water at 5° appears to be $3{\cdot}81 \times 18$; it is obvious from this that the groups must be of varying size, consisting of either four, three, two, or one H_2O: rise of temperature causes a gradual dissociation of the larger groups, so that at no temperature are all the molecules in the liquid uniform so long as molecular aggregation exists at all.

§ 10. Constitutive Properties: Rotation of Polarized Light.

The physical properties so far studied, in this chapter, belong to the class known as *additive*, i. e. the measure of the properties for the entire molecule may be regarded as made up of parts, each of which is peculiar to one atom. Of such properties weight is the typical example, and indeed the only one that is strictly additive. The weight of a molecule is arrived at by adding together the weights of its component parts; the forces between the atoms exercise no influence on the weight to be attributed to each atom. In other cases, e. g. molecular volume, the constitution of the molecule exercises a more or less marked influence, yet the general behaviour is additive: the atoms possess much the same properties as if they were not combined. There are, however, other physical properties which bear an intimate relation to the constitution, so that a comparatively small change in the arrangement of the molecule may alter them entirely. The best instances of such *constitutive* properties are (1) rotation of polarized light, (2) absorption of light with accompanying production of colour.

Ordinary light consists of vibrations at right angles to the direction in which the light is travelling, the direction of the *ray*, such vibrations being called *transverse*. If a plane be drawn at right angles to the ray, the luminous vibration may take place in any manner in that plane, and in general the figure described by a point in the plane will not remain the same for any length of time. By certain devices, however, it is possible to obtain light which retains precisely the same characteristics for any length of time, and which therefore consists of vibrations of a definite and permanent figure. Such light is called *polarized*, and is obtained either by reflection or refraction at certain angles, or more commonly by transmission through a crystal. The simplest kind of polarized light is that in which the figure described by a vibrating point is a straight line merely—the point oscillates to and fro along a short straight line at right angles to the ray. For greater intelligibility let us assume that the ray is travelling vertically upwards (along the axis of a polarizing microscope), that it then encounters a 'polarizer' (Nicol prism, tourmaline plate, &c.). After passing through the polarizer the vibration is exclusively in one direction, say east and west, because the polarizer absorbs any component vibration north and south that the light may previously have possessed. Further on the ray meets an 'analyzer' (another Nicol or tourmaline); if this be placed in the same way as the polarizer, it will allow the east and west vibrations to pass through it unchanged; but if it be rotated 90° it will now only allow north and south vibrations to pass through it, and will consequently absorb all the light that has passed through the polarizer, and the field of view of the microscope will be dark. Light of the kind produced by a Nicol prism or a tourmaline plate is called *plane polarized*, and the plane of polarization is that containing the ray and a certain axis in the polarizer (the longer diagonal of a Nicol prism). Whether the vibrations constituting light are in this plane or at right angles to it, is immaterial; it is sufficient for practical purposes that the plane of polarization can be identified by turning the analyzer till it extinguishes the light, when its axis is at right angles to the plane required, and the analyzer is said to be 'crossed' to the polarizer.

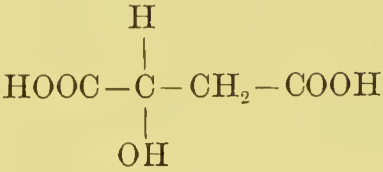
If now certain substances, e. g. quartz, be put between the polarizer and analyzer, the illumination of the field of view is partly restored, but on turning the analyzer through a definite angle it can be extinguished again; this shows that the light on emerging from the quartz is still plane polarized, but the plane has been rotated. The measure of the rotation is easily found if the analyzer be mounted in a graduated circle. It may take place either to the right or to the left, being counted right-handed when, travelling along the ray of light in the direction in which it is going, the rotation is clockwise; or in the previous example, if the light passing vertically upwards is originally polarized east and west, and is rotated through north-east and south-west towards north and south. The angle of rotation is in general different for light of different colours, so that when white light is viewed through a polarizer, a rotating medium, and an analyzer, it is decomposed into colours, a phenomenon known as *rotatory dispersion.* Rotation of the plane of polarization is effected by numerous crystals, and by a certain number of organic substances both pure and in solution, e. g. turpentine, tartaric acid, sugar. It is found that the angle of rotation is proportional to the length of active substance traversed by the beam of light, and when the concentration is variable (as in solutions), to the amount of active material per unit volume. Accordingly the specific rotation $[a]$ may be defined as being, for fixed temperature (20°) and kind of light (sodium light D),

$$[a]_D^{20^\circ} = \frac{a}{lc},$$

where a = observed angle of rotation (in degrees),
l = length of active material (in decimeters),
c = concentration of active material (gms. per c.c.).

In case of a pure substance c becomes identical with the density.

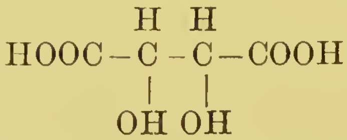
All transparent substances, when placed in a *magnetic field*, are found to rotate polarized light; and this phenomenon, studied especially by W. H. Perkin, has been reduced to atomic values, in the same way as the molecular volume or the refracting power, and therefore belongs to the class of additive properties. But the more interesting case of rotation, which does not require a magnetic field to produce it, and therefore called 'natural' for distinction, occurs only in a small minority of (organic) bodies, and is purely constitutive. It is regularly associated with the pressure of an asymmetrical carbon atom, i. e. a carbon atom connected to four different kinds of atom or atomic group. Thus malic acid has the formula



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{HOOC{-}C{-}CH_2{-}COOH} \\ | \\ \mathrm{OH} \end{array}$$

one of the carbon atoms being connected to the four diverse groups, COOH, H, OH, CH_2COOH, and the substance is accordingly optically active. But the most striking peculiarity is that if a body is optically active at all, there are always at least two isomeric forms of it, which rotate the plane of polarization to right and to left respectively. These forms are usually identical in every other particular, boiling point, density, &c. Van 't Hoff has given the theory of optical isomerism by considering the arrangement of the atoms in space. If a carbon atom be regarded as the centre of a tetrahedron, and the four groups attached to it be arranged at the corners of the tetrahedron, then if all four groups are different, two arrangements are possible, which are not 'congruent,' i. e. one cannot be transformed into the other by any rotation of the figure ; one is, in fact, like the image of the other as seen in a mirror, and these two arrangements constitute the dextro- and laevo-rotatory isomers. But if two of the four groups become identical then the dextro- and laevo- arrangements become identical, for by simply rotating one of them it is seen to coincide with the other. This point cannot be satisfactorily illustrated by diagrams, but is easily demonstrated by a simple model, which may be constructed of a cork with four pins, bearing coloured balls of wax at their ends. The theory is fully confirmed by observation. When an optically active substance is produced in nature by the action of organisms (e.g. in fermentation) often only one isomer is found, but when the compound is produced synthetically the two are always produced together and in equal quantity. The synthetic product (pure or in solution) is therefore a mixture, in which the two components neutralize one another; and it is not possible to separate the two by the usual methods (fractional distillation, fractional crystallization, &c.), because the physical properties of the isomers are the same. But if the compound be crystallized the crystals will often be found to show 'hemihedry,' i.e. a difference in shape, such that one kind is like the reflected image of the other, clearly the effect of the corresponding difference in shape of the molecules: the two kinds of crystals can then be picked out and dissolved separately. The two solutions thus prepared will be found to show right- and left-handed rotation.

When a compound contains two similar asymmetric carbon atoms in the molecule, three isomers are possible: (1) the carbon atoms may both be dextro-rotatory; (2) they may both be laevo-rotatory; (3) one may be dextro- and the other laevo-rotatory. The latter form is inactive, but unlike the mixture of (1) and (2) it cannot be separated into active components, for the compensation takes place within the molecule itself. There are therefore four different forms of the substance. Such a case is tartaric acid,



$$\begin{array}{ccccccc} & & \mathrm{H} & & \mathrm{H} & & \\ \mathrm{HOOC} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{COOH} \\ & & | & & | & & \\ & & \mathrm{OH} & & \mathrm{OH} & & \end{array}$$

which is known as (1) the dextro-, (2) the laevo-rotatory acid, (3) the neutral (undecomposable) form; (4) compound crystals (racemic acid) analogous to a double salt and formed by union of a molecule each of (1) and (2); this form also is neutral to polarized light, but can suffer transition into a mixture of the two active acids.

If light from a luminous flame or an electric lamp be examined by means of a spectroscope, a spectrum is formed, which is a continuous band of colour changing gradually through the various hues from red, orange, yellow, green, and blue, to violet. If now a coloured transparent substance be placed between the light and the spectroscope—a plate of the material if it be solid, a glass cell containing it if it be liquid or in solution—then a part of the original spectrum is found to be absent: the absent portion may be a considerable length in the middle or at one of the ends, or it may consist of dark *bands* of more or less well-defined position. Gases also can be examined in this way, and are found to show dark bands, or, frequently, very narrow and sharply defined dark spaces called lines. In any case the phenomenon indicates that some kinds of light are absorbed by the substance in question, while other kinds are not. The spectrum really extends beyond both the red and violet, only the human eye is not sensitive to radiation beyond those limits. In the infra-red it may be studied by means of a thermopile or bolometer, i. e. a very sensitive thermometric arrangement which absorbs the radiation and is raised in temperature in consequence. In the ultra-violet the radiation is so feeble that it cannot well be measured by any thermometer yet invented, but it produces an effect on a photographic plate held to receive it, and it may be made visible if thrown on a fluorescent screen. In these ways the presence of characteristic absorption lines and bands has been shown in the invisible parts of the spectrum, and frequently a substance which is colourless and transparent, i. e. does not absorb any of the visible rays, is found to give bands in the infra-red or the ultra-violet. The absorption of any kind of light is found to follow the rule

$$I = I_0(1-\gamma)^d,$$

where I_0 = intensity of original light, I = intensity after passing through a layer of thickness d, and γ is a constant, called the coefficient of absorption, i. e. of the original light; the fraction γ is absorbed by passing through 1 cm. of the substance; of that which penetrates the first centimetre the same fraction is absorbed by the next centimetre, and so on. We may say then that the absorption of light by any substance is characterized by a coefficient which has different values for the different kinds of light, and may indeed, in the case of gases with a line spectra, have a very high value for a certain wave length and be zero for another wave length immediately adjacent. The degree of absorption does not in fact vary continuously, as a rule, but occurs in particular parts of the spectrum corresponding to particular modes of vibration of the molecules of the absorbing substance. The modes of vibration are highly characteristic for each substance, and are often entirely altered by a small change in constitution. Thus $N_2 O_4$ is a very slightly coloured gas, but it dissociates into NO_2, a dark brown gas showing a great number of absorption lines in the spectrum. The effect of substitutions has been studied in the case of certain groups of organic substances, and certain empirical rules obtained as to the displacement of the absorption bands. The absorption bands of dye-stuffs dissolved in concentrated sulphuric acid show, in general, a displacement towards the red on introduction of the hydroxyl, methoxyl, methyl, phenyl, and carboxyl groups, and the halogens; while substitution of the nitro- and amido-groups, as well as addition of hydrogen, produces a displacement towards the violet; the effect being more marked the greater the molecular weight of the substituting radicle.

Since many colourless substances possess an absorption band in the ultra-violet, it is possible, by introducing a radicle of the former group, to bring that band into the visible spectrum, say into the violet: the substance then possesses the colour which is obtained by combining all the colours of the spectrum with the exception of violet, a greenish yellow. By means of heavier substituting radicles the band may be made to move lower down the spectrum, and so the colour of the substance may be changed according to a definite sequence. Schütze[1] has worked out an interesting theory of dye-stuffs on that basis.

The physical properties of solids, whether amorphous or crystalline, have not yet been studied to the extent of yielding results of sufficient generality or importance to be quoted in a book like the present.

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[1] *Ostw.* 9. 109.

CHAPTER III

THE PRINCIPLES OF THERMODYNAMICS

[Note.—Throughout this chapter log. means natural logarithm (to the base *e*); common logarithms must be multiplied by 2·3026... to reduce to natural. This must be remembered in working out the examples on pp. 136, 140.]

§ 1. The Laws of Thermodynamics.

There is one group of physical properties, purposely omitted from the preceding chapter, of which the treatment has reached a much more advanced and scientifically intelligible stage than any other; the relations of temperature at which chemical transformations take place, and the quantities of heat involved in those transformations, can be studied under the guidance of definite and general principles, such as are still wanting in regard to the various physical properties so far considered. Temperature and quantity of heat form the subject-matter of that branch of physics known as thermodynamics, or the theory of heat; and thermodynamics is a deductive science. It consists in the analytical development of two principles, known as the first and second laws of thermodynamics, principles which have been established by direct observation, and which there is every reason to believe are universally true. Mathematical deductions can therefore be made from them with perfect certainty and strictness of argument, and the results of experiment may be generalized by means of the deductions obtained. Thermodynamics is, therefore, a subject properly to be compared with dynamics itself, but differs from dynamics in that the dynamical concepts, mass and energy.

are regarded as simple, i. e. not further analyzable, while the thermodynamic concepts, quantity of heat and temperature, are not simple, and indeed not fully understood. For of the two, quantity of heat is energy, but only a special kind of energy which is more readily distinguished from other kinds by its relations to the human senses than by any specifically dynamical property; and temperature, so far as it is understood, appears to be a somewhat recondite dynamical relation (average molecular kinetic energy) of the particular systems which possess the kind of energy known as heat. These conceptions may be dealt with in either of two ways. First we may try to form an approximate idea of the real nature of quantity of heat and temperature, and then apply the usual dynamical methods to those ideas; compare the deductions arrived at with experimental results, and so by successive steps correct the original views as to the structure of the molecular systems considered. That is the method of the molecular or kinetic theory; but, while it has the advantage of offering a closer insight into the properties studied, it is necessarily tentative, and it has the disadvantage of being extremely difficult to carry out mathematically. The second method is to accept the conceptions of quantity of heat and temperature as ultimate, and to accept the two laws with regard to them simply on the basis of observation, and to deduce what is possible from that. This is the method of thermodynamics; it is certain, so far as it goes, and it is mathematically easy; and in the present state of science it is by far the more fruitful and important. Indeed, as applied to chemistry it has of late proved so fruitful that all the leading results in the quantitative study of chemical reactions, together with such phenomena as the change of freezing point and of vapour pressure in solutions, may now be regarded as firmly established on a thermodynamic basis.

An initial difficulty of the subject lies in the variety of ways in which the body of theorems may be presented. The most convenient method seems to be, after a statement of the two laws, to deduce first certain results of the first law of thermodynamics, then to apply these to the properties of a certain ideal substance—a perfect gas—and by that means obtain a quantitative definition of temperature; then by the use of the second law the notion of temperature may be generalized, and an analytical expression given to the second law itself. The rest then follows by simple mathematical methods. This treatment of the subject is essentially that of Clausius, and the present chapter is mainly arranged from the first three chapters of his treatise[1].

The laws of thermodynamics, in the words of Maxwell, are:—

(1) 'When work is transformed into heat, or heat into work, the quantity of work is mechanically equivalent to the quantity of heat';

(2) 'It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature';

—the latter being translated from Clausius' statement. The meaning and importance of these laws will become apparent in the sequel.

§ 2. **The First Law.**

The first law of thermodynamics is merely a particular case of the law of the conservation of energy. The doctrine that the various forms of energy—visible kinetic energy, the energy of gravitating bodies, of elasticity, of electric currents, of chemical affinity, of heat, and so on—are all essentially forms of one quantity, and that that quantity is neither increased nor decreased when one kind is transformed into another, grew up in the middle of this century, supported chiefly by experiments on the conversion of mechanical work into heat. Joule, and others, showed that when in the action of a machine mechanical work is spent without any apparent effect, an amount of heat is produced by friction, compression, or otherwise, which is numerically proportional to the amount of work spent. Hence, it is natural to express the observation in the form given above; the ratio of the work spent to the heat generated is called the dynamical equivalent of heat; the value of it is given in the introduction, but in the equations of the present chapter no mention will be made of it, since any quantity of heat occurring in the equations may be regarded as measured in ergs, and so needs no reducing to dynamical measure. In making numerical applications of the theoretical results, it is sufficient to multiply any quantity of heat that is expressed in calories by the appropriate factor: usually 42,000,000 is a sufficient approximation. The first law of thermodynamics is, however, worth stating independently of the more general law of the conservation of energy, on account of the peculiar position of heat as a mode of energy. For while the mutual convertibility of all the other kinds is subject to no general restrictions, that is not the case with heat. All other kinds of energy can be converted completely into heat, but heat cannot, under any (practically attainable) circumstances, be completely converted in another kind of energy. Hence, for the purposes of thermodynamics, heat must be treated as a distinct quantity.

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[1] Clausius, *Mechanische Wärmetheorie* (ed. 2), 1876.

When heat is imparted to a body it may be used up in two ways: it may remain in the body itself, increasing the stock of energy contained (or *internal energy*), or it may be handed on to some other body in the form of mechanical work, in which case it is said *external work* is done, because the energy is then passed on to a system external to that whose changes are being considered. For example, when heat is imparted by the furnace of an engine to the water contained in its boiler, part of the heat may be spent in increasing the internal energy (in the form of heat) of the water, thus raising its temperature, while—the steam expanding into a cylinder—the remainder is spent in doing mechanical work by means of the piston on some machinery. What becomes of the energy afterwards is immaterial; so far as the *working substance*, the steam, is concerned, it is so much external work done. We are thus able to apply the first law of thermodynamics to the case of any particular body ('working substance') and state it in the form:—

'Heat supplied = increase of internal energy of the working substance + external work done,' or in symbols,

$$Q = U_2 - U_1 + W, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Q = heat supplied to the working substance (measured in dynamical units), U_1 is the internal energy of the working substance before the action considered, U_2 the same after, and W the work done on other bodies.

[With the notation of the calculus it may be put in the differential form $$dQ = dU + dW]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\text{ a})$$

The external work is usually done by effecting some visible motion; in the last chapter of this book certain electrical cases will be considered, but with that exception the external work will always be work done against a fluid pressure. Thus, if a fluid (the steam in the former example) enclosed by a piston expand, the work done is measured by the product of the force exerted on the piston into the distance the latter moves; but the force is equal to the fluid pressure applied multiplied by the area of the piston, and the area multiplied by the distance through which the piston moves is the increase of volume of the fluid. Hence we arrive at the result that:—

'Work done by a fluid in expanding against a pressure equal to its own = the pressure × increase of volume of the fluid.'

If v_1 be the volume of the fluid before the expansion, and v_2 after, p the pressure, then

$$W = p\,(v_2 - v_1).$$

(The pressure may not remain the same during the expansion, but if not p must be regarded as the mean pressure.) Hence we may write the first law of thermodynamics for such systems as—

$$Q = U_2 - U_1 + p\,(v_2 - v_1), \quad . \quad . \quad . \quad . \quad (2)$$

[or

$$dQ = dU + pdv, \quad . \quad . \quad . \quad . \quad . \quad (2\,\text{a})$$

for an infinitesimal expansion, and if p varies with v in any known manner this may be integrated accordingly.]

The internal energy of such a system consists of two parts: (1) the heat or *temperature energy*, i. e. the energy of motion of its molecules; (2) the *volume energy* or potential energy it possesses on account of forces between the molecules. The amount of the former is defined by the temperature of the fluid, that of the latter by its volume. The volume energy (part of the internal energy of the fluid itself) must be carefully distinguished from the external work done in change of volume, $p\,(v_2 - v_1)$. We shall see immediately that a perfect gas possesses no volume energy, since there are no forces between its molecules; but this, of course, does not imply that it is incapable of doing work on expansion, for such work may be done at the expense of its temperature energy.

[In mathematical language the distinction is expressed by writing the total variation of internal energy[1]—

$$\delta U = \frac{\partial_v U}{\partial T}\,\delta T + \frac{\partial_T U}{\partial v}\,\delta v.]$$

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[1] The symbol $\frac{\partial_y z}{\partial x}$ means the partial differential coefficient of z with respect to x taken on the assumption that y is constant.

§ 3. Application to a Perfect Gas.

The next step is to apply this law to the ideal substance known as a perfect gas, the ideal to which the actual gases approximate. The properties of a perfect gas are:

(1) Its characteristic equation is of the form

$$pv = RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(see introduction); or in other words, it obeys the laws of Boyle and Gay-Lussac.

(2) Its internal energy is independent of its volume. This was first proved by an experiment of Joule, in which he allowed air to expand from one vessel in which it was compressed into another which was evacuated. No work was done by the gas in expanding, since there was no counter-pressure for it to overcome; no heat was communicated to it during the expansion, hence its internal energy must have remained the same. But observation showed that the temperature of the gas was unaltered. Now, as the total internal energy remained the same, its volume energy could only have increased (or decreased) in consequence of a decrease (or increase) in its heat energy; the absence of change in temperature therefore proves that the change in volume does not occasion any change in energy.

$$\left[\text{That is, } \frac{\partial_T U}{\partial v} = 0 \text{ for a perfect gas.}\right] \quad . \quad . \quad . \quad (4)$$

We may now define a scale of temperature, for if a perfect gas be heated in an inexpansible vessel, then setting v constant in the characteristic equation we have

$$p \propto T,$$

i. e. the pressure is proportional to the (absolute) temperature, and may be taken as a measure of it; similarly, if the gas be heated at constant pressure, the volume is proportional to the temperature. In either of these ways a gas thermometer is employed to determine temperature, and it is found that the melting point of ice is very close to 273° on the gas scale, the interval between the melting and boiling points being taken as 100°.

Suppose then a gram-molecule of a perfect gas be heated through a range of 1° while its volume is kept constant; the amount of heat absorbed, say K_V, is the molecular *specific heat at constant volume.* But if it be heated through 1° at constant pressure, p, it will expand by an amount $= \frac{v}{T}$, where v, T are the original volume and temperature: it accordingly does external work to the amount of $p \times \frac{v}{T}$. The increase of its volume energy, as we just saw, is nil, consequently the heat absorbed must be as much as before, plus that required to effect the work $\frac{pv}{T}$. Calling the quantity K_P the molecular *specific heat at constant pressure,* we have

$$K_P = K_V + \frac{pv}{T},$$

or by the characteristic equation

$$K_P = K_V + R. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The ratio $\frac{K_P}{K_V}$, which is important, will be expressed by the symbol G.

Hence the specific heat at constant pressure is greater than that at constant volume by the amount $R = 1{\cdot}98$ calories per gram-molecule for any gas that is approximately perfect.

When a gas expands under the condition of constant temperature (isothermal condition) $p = \frac{RT}{v}$, where RT is a constant; hence, to find the heat absorbed during a finite expansion v_1 to v_2, we have

$$\int dQ = \int_{v_1}^{v_2} \frac{RT\,dv}{v} + \int dU = RT \log \frac{v_2}{v_1} + \int dU\,;$$

but dU is zero, since the temperature does not change, and U is for a gas independent of the volume. Therefore the heat absorbed

$$Q = RT \log\left(\frac{v_2}{v_1}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

There remains another important case of expansion, viz. that in which no heat is imparted to or withdrawn from the expanding fluid; it is called *isentropic.* This case is nearly realized when steam expands very rapidly in the cylinder of an engine, for the operation is too rapid to allow much communication of heat to or from the walls of the cylinder.

In this case

$$dQ = 0 = dU + \frac{RT}{v} dv,$$

or

$$0 = K_V dT + (K_P - K_V) \frac{T}{v} dv,$$

or

$$\frac{dT}{T} + (G-1) \frac{dv}{v} = 0,$$

which gives on integration

$$\frac{T_2}{T_1} = \left(\frac{v_2}{v_1}\right)^{1-G},$$

and by means of the characteristic equation

$$\frac{T_2}{T_1} = \left(\frac{v_2}{v_1}\right)^{1-G} = \left(\frac{p_2}{p_1}\right)^{\frac{G-1}{G}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence the work done by the gas in expanding isentropically from v_1 to v_2 is

$$W = \int_{v_1}^{v_2} p dv = p_1 v_1^G \int_{v_1}^{v_2} \frac{dv}{v^G} = \frac{p_1 v_1^G}{G-1} \left(\frac{1}{v_1^{G-1}} - \frac{1}{v_2^{G-1}}\right)$$

$$= \frac{p_1 v_1}{G-1} \left\{1 - \left(\frac{v_2}{v_1}\right)^{1-G}\right\},$$

or by means of the preceding equation (7)

$$W = \frac{RT_1}{G-1}\left(1 - \frac{T_2}{T_1}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where T_1, T_2 are the temperatures possessed by the gas at the beginning and end of the expansion respectively.

§ 4. Reversibility.

The processes just considered belong to the class known as *reversible.* If during the expansion of a gas its temperature be maintained constant, heat must be supplied to it to the extent just calculated; for that purpose a source of heat must be available whose temperature is higher than that of the working substance, in order that heat may flow by conduction. But the source need not exceed the working substance in temperature by a finite amount; any excess, however small, will suffice to make the heat flow, though more slowly the smaller the difference of temperature. Similarly, if it be desired to compress the gas again without allowing its temperature to rise, heat must be withdrawn from it, i. e. it must be placed in communication with a body of lower temperature, to serve as a receiver of heat; but, again, the receiver may be as little as we please cooler than the working substance. Hence, to reverse such an isothermal process, it is only necessary to change the temperature of the external body, which serves as source or receiver, from a little warmer to a little cooler than the working substance. Perfect reversibility would be the ideal limiting case in which the change of temperature was vanishingly small. Such reversibility is, of course, unattainable in practice in an actual steam engine, e. g. the time available for heating and cooling is short, so that the steam must be heated by means of furnace gases which are hundreds of degrees hotter; the heating is therefore irreversible: the heat cannot be made to flow back into the furnace gases by reversing the motion of the piston. Similarly, with regard to the transfer of mechanical energy in expansion, we have to distinguish the limiting case of reversibility from the actual one of irreversibility. The limiting pressure against which a fluid can expand is equal to its own pressure; if the pressure resisting the expansion be less, the expansion will take place more rapidly, but less work will be done; and in order to reverse the process and compress the fluid, the external circumstances will have to be altered to a finite extent, the pressure which was less than that of the fluid being made greater. The expansion will therefore only be reversible when the pressure applied to the fluid (say, by a piston) is constantly equal to the pressure of the fluid itself; the expansion of steam in a cylinder approaches this condition as nearly as the speed of working required allows, while the extreme case of irreversibility is seen in the experiment of Joule mentioned above, in which air was allowed to expand into a vacuum. There no work at all was done, since there was no counter-pressure to overcome, and the process could only be reversed by an entire change in the circumstances of the gas. The calculations given above for the work done in isothermal and isentropic expansion apply, it must be noted, only to reversible expansions, and consequently give the *maximum work* which can be done by the expanding gas.

'A process that can in no way be completely carried out backwards is called irreversible, all other processes reversible. That a process may be irreversible it is not enough that it cannot be directly reversed—that is the case with many mechanical processes that are not irreversible—but it is required that, even with the aid of all the resources occurring in nature, no means exist by which, after the process has taken place, the initial conditions may be exactly restored' (Planck).

§ 5. Entropy of a Perfect Gas.

The volume of a fluid, and its internal energy, are both quantities which are completely definite when the pressure and temperature of the fluid are defined: if a fluid pass from one state, defined by the co-ordinates p_1 T_1, to another defined by p_2 and T_2, its volume changes at the same time from a certain value v_1 to v_2, no matter what intermediate states may be passed through; and the same is true of the internal energy, which may change from U_1 to U_2 by a definite amount. Briefly, the volume and energy of a fluid are functions of its co-ordinates. There is another quantity, also a function of the co-ordinates, which is somewhat obscure in its nature, and difficult to grasp, but which is extremely important for the theory of heat, and offers the simplest and clearest mode of expression of the second law of thermodynamics: this function is the *entropy.* To arrive at a notion of its meaning, we will first consider the processes already described as isentropic, i. e. of constant entropy. Such a process consists in a reversible expansion or compression in which no heat is supplied to or withdrawn from the working substance. If then we begin by defining the entropy as a quantity which remains constant during an isentropic process, we may deal first with a perfect gas and make use of the equation

$$Q = d\,U + pdv = 0,$$

or

$$K_V dT + \frac{RT}{v} dv = 0,$$

which on integration gives

$$K_V \log T + R \log v = \text{constant}.$$

This then is a quantity whose value remains unchanged during the expansion, and if we assume that the entropy of a perfect gas

$$S = K_V \log T + R \log v + \text{constant},$$

we shall satisfy the conditions so far laid down.

The constant is arbitrary, and must be found by defining some standard condition of zero entropy: the condition may conveniently be that defined by the freezing point (T_0)

and atmospheric pressure (p_0), so that if v_0 is the molecular volume under those conditions, the entropy of a perfect gas is given by

$$S = K_V \log \frac{T}{T_0} + R \log \frac{v}{v_0} \cdot \quad . \quad . \quad . \quad . \quad (9)$$

Example. To find the entropy of saturated carbon dioxide vapour at 20°. The saturation pressure at that temperature is 59 atmos. The specific heat at constant volume is 0·154 calories per gram, i.e. $0{\cdot}154 \times 44$ per gm. molecule, and $R = 1{\cdot}98$ calories. The volume v may be calculated on the assumption that the gas is perfect, as $v = v_0 \times \frac{293}{273} \times \frac{1}{59}$. Hence

$$S = 0{\cdot}154 \times 44 \log \tfrac{293}{273} + 1{\cdot}98 \log \frac{293}{273 \times 59} = -\ 7{\cdot}453,$$

the unit of energy being the calorie. This is the *molecular* entropy.

From the expression for the entropy it follows that in passing from the condition (v_1, T_1) to (v_2, T_2) a gas increases in entropy from

$$S_1 = K_V \log\left(\frac{T_1}{T_0}\right) + R \log\left(\frac{v_1}{v_0}\right)$$

to

$$S_2 = K_V \log\left(\frac{T_2}{T_0}\right) + R \log\left(\frac{v_2}{v_0}\right),$$

whence

$$S_2 - S_1 = K_V \log\left(\frac{T_2}{T_1}\right) + R \log\left(\frac{v_2}{v_1}\right) \cdot \quad . \quad . \quad (10)$$

The quantity thus defined has obviously a definite value when v and T (or p and T) are given: it is therefore a 'function of the co-ordinates'; the next point is to show in what relation it stands to reversible and irreversible changes. (1) In an isentropic (reversible) change the heat communicated to the working substance is zero, so that no change of entropy implies no communication of heat (in a reversible process). (2) In an isothermal (reversible) process the heat communicated according to (6) is

$$Q = RT \log\left(\frac{v_2}{v_1}\right),$$

but the increase of entropy is by (10)

$$S_2 - S_1 = R \log\left(\frac{v_2}{v_1}\right),$$

so that

$$S_2 - S_1 = \frac{Q}{T}. \quad \ldots \ldots \quad (11)$$

But any change whatever may be accomplished by means of successive steps which are either isentropic or isothermal, so that as the entropy of the gas in any given condition is the same, by whatever means that condition is arrived at we may conclude generally that:—

'When a perfect gas suffers any reversible change, the increase in its entropy is found by dividing each quantity of heat communicated by the temperature at which it is received, and adding together the quotients so obtained.'

Or symbolically

$$dS = \frac{dQ}{T}; \quad \ldots \ldots \quad (11\,a)$$

but in a reversible change we have seen that

$$dQ = dU + pdv;$$

therefore

$$dS = \frac{dU + pdv}{T},$$

and

$$\left[S\right]_1^2 = \int_1^2 \frac{dU + pdv}{T}.$$

The next step is to show that the quantity thus found—the entropy—is the criterion of the possibility of change in a system of perfect gases; but to this end a system must be considered, such that no outstanding effects remain in other bodies, in other words an *isolated* system. Imagine two gases separated by a partition that allows free passage of heat from one to the other, but prevents equalization of pressure, and let the system be isolated from any surroundings. Then a reversible change might occur in which one of the gases expanded while the other contracted. Suppose that during the process a quantity of heat Q_1 is converted into work in the first gas, while in the second a quantity Q_2 is evolved at the expense of work. Since the process is reversible the quantities of work must be equal, and therefore $Q_1 = Q_2$, and this amount of heat will simply flow through the partition from the contracting gas to the expanding. The former therefore loses entropy to the extent $\frac{Q_1}{T}$, while the latter gains $\frac{Q_2}{T}$, where T is the common temperature of the two gases, and these two quantities are equal, so that the total entropy is unchanged.

Here we have an instance of a reversible process, and the accompanying change of entropy is zero: the same may be shown to be true of any other instance, and we may conclude that *in any reversible change of an isolated system of perfect gases the total entropy remains constant.*

Next, if the change is irreversible. As a type of this, consider Joule's experiment in which a gas expands into a vacuum; the system is isolated, for no communication of heat takes place even if no precautions are taken against it, the temperature of the gas remaining the same during the expansion. The change of entropy may be calculated from

$$S = K_V \log\left(\frac{T}{T_0}\right) + R \log\left(\frac{v}{v_0}\right),$$

and since T remains the same while v increases, it is obvious that the entropy must increase. There is however no means of reversing the process and restoring the gas to the smaller volume without the interference of some external agency, i. e. the converse process which involves a decrease in the entropy of an isolated system is impossible. This argument too may be extended to the consideration of other cases, and leads to the very important conclusion that *any action of an isolated system of perfect gases leads to an increase in the total entropy of the system*, except in the limiting case of reversible action in which the entropy remains constant.

§ 6. Entropy as the Criterion of Equilibrium in general.

Thus far in developing an expression for the entropy, and in considering the relations between that quantity and the equilibrium of the system concerned, we have dealt only with perfect gases. The same arguments may, however, be extended to cover any substance whatever. It is true that we cannot always find an explicit expression for the entropy, because to do so requires a knowledge of the characteristic equation of the substance, and the characteristic equation is only known approximately, if at all, for real substances. To find the general condition of equilibrium, however, does not require any such detailed knowledge. It may be shown that there always is a function possessing the same properties as the entropy of a gas: a function defined by the condition that if the body goes through a *reversible* process in which it absorbs a quantity of heat, Q, while its temperature is T, then

$$\frac{Q}{T} = S_2 - S_1,$$

the increase in the value of the function between the beginning and end of the process. This function is called the entropy of the substance, and plays the same part with regard to equilibrium as in gases. Here the temperature is to be measured on the gas scale, so that the temperature as calculated from the properties of a perfect gas really possesses a meaning which is independent of the properties of any special substance; for this reason the term *absolute* *scale of temperature* has been adopted. The absolute scale is very nearly rendered in practice by the indications of a constant-volume hydrogen thermometer.

Example. To calculate the entropy of liquid carbon dioxide at 20°.

That of the saturated vapour was shown above to be $-7{\cdot}453$: in condensing the vapour gives out 34 calories per gram, that being the latent heat of carbon dioxide at 20°, or 34×44 per gram-molecule. Hence it loses entropy to the extent $\frac{34 \times 44}{293} = 5{\cdot}106$. Therefore the molecular entropy of the liquid is $-7{\cdot}453 - 5{\cdot}106 = -12{\cdot}559$.

Now although the entropy has been defined by means of the quantity of heat absorbed in a reversible change, no restriction is implied as to the application of the results obtained. For the entropy of a substance depends exclusively on its condition at the moment considered; that condition defined, say, by means of the pressure and temperature, the value of the entropy is fixed, just as that of the volume of the body is fixed, no matter whether the condition has been arrived at by reversible or irreversible processes. For instance, the entropy of carbon dioxide in the liquid state at 20° has been calculated above by means of reversible processes; but should liquid carbon dioxide at 20° be allowed to evaporate *in vacuo,* and then be cooled by contact with melting ice—both of which processes are irreversible—till it is at 0° C. and one atmosphere pressure, its entropy would be $-12{\cdot}559$ in the first state, and 0 in the last, so that the change in entropy would be the same as in the reversible path between the same initial and final states.

The entropy of any substance (referred to the same substance in some standard condition as zero) may, then, be calculated if only sufficient experimental data exist, although the form of the equation connecting the entropy with pressure and temperature is not as a rule known. The quantity calculated in the numerical examples above is properly called the molecular entropy, i. e. the entropy per gram-molecule of material. The total entropy of a body may easily be found by multiplying its molecular entropy by its mass expressed in mols.; and the total entropy of a system is the sum of the entropies of the separate parts.

Next, reasoning with the aid of the results for perfect gases, already obtained, it may be shown that any reversible process in an isolated system leaves the total entropy of the system unchanged, while an irreversible process causes it to increase. We have therefore arrived at a universal criterion of the possibility of change, or in other words a universal criterion of equilibrium. This may be put as follows:—

'*An isolated system is in equilibrium when any possible change in it causes its total entropy to increase.*'

Or,

'*The entropy of an isolated system tends to a maximum.*'

Symbolically this may be expressed by saying:—

'If S be the total entropy of an isolated system, then, according as $\delta S <$ or > 0 for any process, that process will be (1) impossible, (2) possible but irreversible. If $\delta S = 0$ the process belongs to the limiting (and practically unattainable) class of reversible actions.'

This then is the mathematical expression of the second law of thermodynamics. Any problem in thermodynamics may be solved by means of it and the equation to the first law already obtained.

§ 7. Deduction of the Law of Mass Action.

Despite the great place occupied by thermodynamic reasoning in theoretical chemistry, and the variety of special cases to which it has been applied with success, there are practically only two theorems involved. These are on (1) the chemical equilibrium in a system of perfect gases maintained at constant temperature; (2) the influence of temperature upon chemical equilibrium. These two theorems have proved so fruitful that, either by their direct application or by analogy, they allow of systematizing nearly all the phenomena of chemical dynamics.

The first of the two is to a certain extent identical with the empirical law stated by Williamson, and by Guldberg and Waage, as to the influence of mass on chemical equilibrium; but while a strict thermodynamic proof may be given in the limiting case of gases treated as perfect gases, no indication is given by the thermodynamic reasoning as to what error is involved in applying the law to actual gases at considerable concentration. Experiment shows—as we shall see in the following chapter—that it is practically true for gases, and by analogy, for solutions over somewhat wide limits of concentration.

As applied to gases it may be expressed in the following way:—

Let there be a mixture of gases A, B, C, D . . . between which the reaction

$$\nu_A A + \nu_B B + \ldots = 0$$

can take place. (Here for convenience all the terms are put on the left-hand side, with positive or negative sign as required, ν_A, ν_B, &c., being whole numbers. E.g. the formation of steam from oxygen and hydrogen would be written $-2\,H_2 - O_2 + 2\,H_2O = 0$, so that in that case $\nu_A = -2$, $\nu_B = -1$, $\nu_C = +2$, there being an increase in the quantity of steam, and a decrease in that of hydrogen and oxygen.)

Let the concentrations in mols. per c.c. be C_A, C_B . . . *Then the product of the concentrations, each raised to a power* *equal to the number of molecules of its own kind occurring in the reaction, is constant.* Or

$$C_A^{\nu_A} \times C_B^{\nu_B} \times \ldots = K. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

E. g. in the equilibrium between hydrogen, oxygen, and steam at high temperatures

$$C_{\mathrm{H_2}}^{-2} \times C_{\mathrm{O_2}}^{-1} \times C_{\mathrm{H_2O}}^{+2} = K.$$

Here K is called the *reaction constant.*

The law is often expressed in the corresponding logarithmic form,

$$\nu_A \log C_A + \nu_B \log C_B + \ \ldots \ = \log K,$$

or briefly

$$\Sigma \nu \log C = \text{const.} \quad . \quad . \quad . \quad . \qquad (12\,\text{a})$$

The reaction constant is a quantity which might be calculated from a sufficiently complete knowledge of the thermal properties of each gas of the system; but practically it is determined by experiments on the equilibrium between the gases. To prove the law we have to show that if in a mixture of gases the concentrations are in agreement with the equation just stated, then a small change made in accordance with the conditions of the system will not occasion any change in the entropy of the system. Such a change will be the conversion of a small amount of the reacting gases according to the equation

$$\nu_A A + \nu_B B + \ldots = 0.$$

Since we desire to obtain the condition of equilibrium at constant temperature, and the reaction is (in general) accompanied by an evolution of heat (+ ve or − ve), we may suppose the reacting system placed in thermal communication with a *reservoir* of heat (say a mass of melting solid) capable of absorbing (reversibly) all the heat generated without changing its temperature T, which is also the temperature of the reacting gases. We shall then be dealing with an isolated system, and can apply the condition of maximum entropy.

In 1 c.c. we have of the first gas C_A mols., therefore its molecular volume (dilution) is $= \frac{1}{C_A}\cdot$ Inserting this in the expression for the entropy of a gas, we have for the molecular entropy

$$s_A = K_{V_A} \log \frac{T}{T_0} + R \log \frac{1}{C_A v_0}; \quad . \quad . \quad . \quad (13)$$

but since the temperature is constant throughout we need not write this expression out at length, but put

$$s_A = j_A - R \log C_A.$$

Of this gas there is a quantity C_A mols., so that it has on the whole the entropy

$$s_A = C_A (j_A - R \log C_A);$$

the total entropy of the mixture (per c.c.) is therefore

$$S' = \Sigma C (j - R \log C).$$

Next suppose that a small quantity of the gas is transformed according to the reaction considered, so that δC_A mols of A are produced, δC_B mols. of B, and so on, while the volume of the gas remains unaltered. Then the entropy of the gas will change from two causes: (1) the quantity of A present will alter (increase or decrease according to the part the gas A plays in the reaction), and so with the others; (2) the new quantity of A will still occupy 1 c.c., so that its concentration will be greater or less than before, and therefore its molecular entropy less or greater than before. Both these changes are taken into account in differentiating a product of two factors, and we get for the increase in entropy *of the gas*

$$\delta S' = \Sigma (j - R \log C) . \delta C + \Sigma C . \delta (j - R \log C);$$

but since j is a constant, this

$$= \Sigma j . \delta C - R \Sigma \log C . \delta C - R \Sigma C \cdot \frac{\delta C}{C}$$

$$= \Sigma (j - R) . \delta C - R \Sigma \log C . \delta C,$$

R being put outside the sign of summation, since it is the same for all gases.

Now the quantities δC_1, δC_2, &c., taking part in the reaction, are proportional to the whole numbers ν_1, ν_2, &c., or say $\delta C_1 = \nu_1 \delta\gamma$, and so on. Then we may write

$$\delta S' = \Sigma\,(j-R)\,\nu\,.\,\delta\gamma - R\Sigma\nu \log C\,.\,\delta\gamma.$$

To this must be added the increase of entropy *of the reservoir*; the latter absorbs the quantity $q\,.\,\delta\gamma$ of heat that is liberated, hence its increase of entropy is $\delta S'' = \frac{q\,\delta\gamma}{T}$; and adding together the two increases dS' and $\delta S''$ we get the total increase of entropy *of the system*

$$\delta S = \left(\Sigma\,(j-R)\nu - R\Sigma\nu \log C + \frac{q}{T}\right)\delta\gamma.$$

Hence for equilibrium we must have

$$\Sigma\,(j-R)\,\nu - R\Sigma\nu \log C + \frac{q}{T} = 0, \quad . \quad . \quad (14)$$

but since the first and third terms on the left-hand side are independent of the concentrations, we may divide by R and write the condition that must hold between the concentrations

$$\Sigma\nu \log C = \text{constant}.$$

Guldberg and Waage's law is thus established for the case of a mixture of perfect gases; its meaning will be elucidated in the following chapters, where repeated applications to experimental cases will be made.

§ 8. **Thermodynamic Equation between p, v, S, and T.**

The second thermodynamical theorem which is of importance for theoretical chemistry is based upon a certain relation that exists between the pressure, volume, temperature, and entropy of any substance; or, in other words, between the first three of these quantities, and the heat involved in a change in the condition of the substance. As stated by Maxwell the relation is as follows :—

'The latent heat of expansion is equal to the product of the absolute temperature and the increment of pressure per degree of temperature at constant volume.'

The meaning of this is perhaps more easily grasped if it be expressed symbolically. By latent heat of expansion is meant the heat absorbed when one gram-molecule of the substance expands by one cub. cm. ; the expansion may be due to a fall of pressure, or to change of state from solid to liquid or liquid to vapour (in this case the heat is commonly spoken of as becoming 'latent'), or to chemical reaction accompanied by change of volume. If for any of these causes an amount of heat Q is absorbed by one mol., whilst it expands from v_1 to v_2, the latent heat of expansion is measured by $\frac{Q}{v_2-v_1}$. Again, if the substance is heated from T_1 to T_2, not being allowed to expand, and in consequence rises in pressure from p_1 to p_2, the increment of pressure per degree is $\frac{p_2-p_1}{T_2-T_1}$. The relation, therefore, is that

$$T \times \frac{p_2-p_1}{T_2-T_1} = \frac{Q}{v_2-v_1}.$$

Here T may conveniently be regarded as the mean between T_1 and T_2, but those two temperatures must not be far apart.

More strictly we may write the equation in the differential form

$$T\frac{\partial_v p}{\partial T} = \frac{\partial_T Q}{\partial v},$$

but since $dQ \div T = dS$, this is

$$\frac{\partial_v p}{\partial T} = \frac{\partial_T S}{\partial v}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

(The notation used is that of Clausius, in which the independent variable which is to be regarded as constant is expressed by a suffix to the sign, ∂, of partial differentiation.)

To prove the relation the most convenient way is to consider the variations of the quantity $U - TS$. This, which will be written F, has been variously called the 'free energy,' or 'available energy,' or 'thermodynamic potential at constant volume.' F is a quantity of energy (for U is the internal energy of the substance, and the other term TS represents a certain quantity of heat), and, moreover, it is a quantity which is definite and always the same for a given substance in a given state, since U, T, and S are all definite in amount for any given state of the substance. Now any variation of the quantity F may be expressed by

$$dF = dU - d(TS) = dU - TdS - SdT,$$

according to the well-known theorem on the differentiation of a product. But

$$TdS = dU + pdv$$

(cf. p. 137); hence we may put

$$dF = dU - SdT - (dU + pdv) = -SdT - pdv, \quad . \quad (16)$$

and regarding T and v as the independent variables

$$\frac{\partial_v F}{\partial T} = -S \text{ and } \frac{\partial_T F}{\partial v} = -p.$$

But since F is a function of the variables T and v, we know from the calculus that

$$\frac{\partial}{\partial v}\frac{\partial F}{\partial T} = \frac{\partial}{\partial T}\frac{\partial F}{\partial v}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

hence

$$\frac{\partial_T S}{\partial v} = \frac{\partial_v p}{\partial T},$$

the result to be proved.

(This result may be illustrated graphically by Fig. 22, in which pressure and volume of the substance are represented by ordinate and abscissa. The free energy F of the substance when in the condition A is represented by the shaded area OAM bounded by the line of constant volume AM, the line of constant temperature AO, and the lines of zero pressure and of zero entropy. If the state of the body is changed by a small amount, from A to B, the free energy is increased by the area QBDO, and decreased by the area ADNM. A change effected at constant temperature is shown by AD, and is accompanied by a decrease of free energy ADNM $= pdv$, so that $\frac{\partial_T F}{\partial v} = -p$. A change effected at constant volume is shown by AC, and is accompanied by an increase in free energy QBDO $= SdT$; but as S has a negative value to the left of QO, it follows that $\frac{\partial_v F}{\partial T} = -S$. Further, both

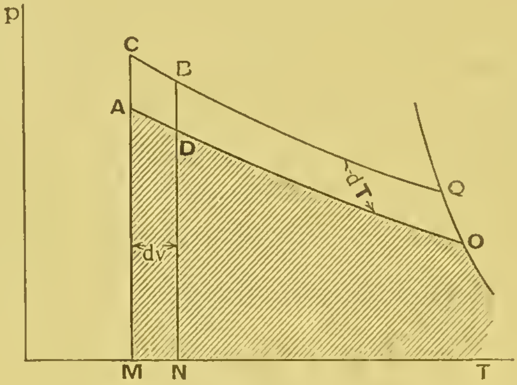

FIG. 22.

$$\frac{\partial}{\partial T}\frac{\partial F}{\partial v}\,dvdT \text{ and } \frac{\partial}{\partial v}\frac{\partial F}{\partial T}\,dTdv$$

are represented by the area ACBD, and so are obviously identical.)

§ 9. Deduction of the Influence of Temperature on Equilibrium.

The thermodynamic equation just proved may be applied to two groups of cases: (1) discontinuous changes, (2) reactions in a homogeneous system. With regard to the former, which includes fusion, evaporation, sublimation, and a certain class of chemical changes which are accompanied by an abrupt change of physical state, such as from rhombic sulphur to the other crystalline form of the same substance, the application is quite straightforward, and will be considered in detail in chap. vi. On the other hand, the application to the changes accompanying reaction in a gas or dilute solution, for which Guldberg and Waage's law holds, may most conveniently be formulated with the aid of the reaction constant as follows :—

Let E_A, E_B, &c., be the quantities (in gram-molecules) of the gases $A\ B\ .\ .\ .$ present originally in v c.c., and let the reaction

$$\nu_A A + \nu_B B + \ldots = 0$$

take place between them to the extent γ, i. e. $\nu_A \gamma$ gram-molecules of A are formed, $\nu_B \gamma$ of B, and so on ; γ may be called the *degree of reaction* by analogy with the degree of dissociation. We have to evaluate the two equal quantities $\frac{\partial S}{\partial v}$ and $\frac{\partial p}{\partial T}$. Now when the system of gases expands by a small amount the degree of reaction is altered, and in order to keep up its temperature it must be supplied with heat, (1) to supply the increase of internal energy consequent on the reaction proceeding further ; (2) to do external work. Or,

$$dQ = -q \frac{\partial_T \gamma}{\partial v} dv + p dv,$$

where q is written for the 'heat of reaction,' i.e. the decrease of internal energy due to reaction between the quantities of the reagents occurring in the equation.

Hence, as

$$dS = \frac{dQ}{T},$$

$$\frac{\partial_T S}{\partial v} = -\frac{q}{T} \frac{\partial_T \gamma}{\partial v} + \frac{p}{T}.$$

Again, if the system of gases is raised in temperature while its volume is kept constant, its pressure rises (1) by the direct effect of temperature on the pressure of each gas; (2) because the degree of reaction is altered, and therefore the number of molecules present. Or,

$$\frac{\partial_v p}{\partial T} = \frac{p}{T} + \frac{\partial_v p}{\partial \gamma} \cdot \frac{\partial_v \gamma}{\partial T}.$$

Comparing the last two equations we get

$$-\frac{q}{T} = \frac{\partial_T v}{\partial \gamma} \times \frac{\partial_v p}{\partial \gamma} \times \frac{\partial_v \gamma}{\partial T}. \quad . \quad . \quad . \quad (18)$$

This expression takes a simpler form if, instead of the degree of reaction, the *reaction constant* K be introduced; the latter is defined by

$$\log K = \Sigma \nu \log C = \Sigma \nu \log \frac{E + \nu\gamma}{v}.$$

Differentiating this equation under the condition of constant temperature, and therefore constant K, we have

$$\Sigma \frac{\nu^2 d\gamma}{E + \nu\gamma} - \frac{dv}{v} \Sigma \nu = 0,$$

whence

$$\frac{\partial_T v}{\partial \gamma} = \frac{v \Sigma \dfrac{\nu^2}{E + \nu\gamma}}{\Sigma \nu}.$$

Further, since $\Sigma \nu$ represents the increase in the number of molecules due to the reaction,

$$\frac{\partial_T p}{\partial \gamma} = \frac{RT}{v} \Sigma \nu$$

by the characteristic equation to a gas.

Lastly, from

$$\log K = \Sigma \nu \log \frac{E + \nu\gamma}{v},$$

if $v =$ constant we get

$$\frac{\partial_v \log K}{\partial T} = \Sigma \frac{\nu^2}{E + \nu\gamma} \cdot \frac{\partial_v \gamma}{\partial T} \text{ or } \frac{\partial_v \gamma}{\partial T} = \frac{\dfrac{\partial_v \log K}{\partial T}}{\Sigma \dfrac{\nu^2}{E + \nu\gamma}}.$$

Introducing these three results into the expression (18) for $\frac{q}{T}$,

$$-\frac{q}{T} = \frac{v\Sigma\frac{\nu^2}{E+\nu\gamma}}{\Sigma\nu} \times \frac{RT}{v}\Sigma\nu \times \frac{\frac{\partial_v \log K}{\partial T}}{\Sigma\frac{\nu^2}{E+\nu\gamma}} = RT\frac{\partial_v \log K}{\partial T}. \quad (19)$$

This may be regarded either as an equation for determining the heat of reaction q, if the reaction constant K has been measured at more than one temperature; or for calculating the effect produced by change of temperature on the reaction constant, if the heat of reaction be known. Numerous examples of its use will be given below.

§ 10. Alternative Deduction.

In the preceding section we have given, on account of its important place in the history of theoretical chemistry, a proof of the theorem on the influence of temperature on equilibrium, substantially identical with that adopted by van 't Hoff, to whom the theorem is originally due. Instead, however, of basing the proof on the thermodynamic relation, we may follow up directly the reasoning of § 7 and obtain an easier deduction. The former method brings the law of temperature-influence into its natural relation with the influence of temperature on discontinuous changes; the present method illustrates its equally natural relation with the law of mass action.

The proof is as follows:—

In equation (14) the quantity j is an abbreviation, having the meaning

$$j = K_V \log\frac{T}{T_0} - R\log v_0$$

(see equation (13)). Restoring the full expression to (14) we get

$$\log T \,.\, \Sigma K_V v - \log T_0 \,.\, \Sigma K_V v - R \log v_0 \,.\, \Sigma v - R \,.\, \Sigma v$$
$$- R \,.\, \Sigma v \log C + \frac{q}{T} = 0. \quad . \quad . \quad (20)$$

Differentiating with respect to T

$$\frac{\Sigma K_V v}{T} - R \frac{d}{dT} \Sigma v \log C - \frac{q}{T^2} + \frac{1}{T} \frac{dq}{dT} = 0.$$

Now q is the heat of reaction at constant volume, i.e. the *decrease* of internal energy due to the reaction, or say $q = U - U'$, where U is the internal energy of the substances disappearing in the reaction, U' of the substances formed. Hence $\frac{dq}{dT}$ will be the difference between the rates of increase with temperature of U and U' respectively; but the rate of increase of internal energy is the thermal capacity at constant volume expressed for each substance by $K_V v$. Hence $\Sigma K_V v = \frac{dq}{dT}$, and the equation reduces to

$$- R \frac{d}{dT} \Sigma v \log C - \frac{q}{T^2} = 0.$$

Remembering the definition of the reaction constant K this may be written

$$- \frac{q}{T^2} = R \frac{\partial_v \log K}{\partial T}, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

identical with (19).

CHAPTER IV

CHEMICAL DYNAMICS OF HOMOGENEOUS SYSTEMS

§ 1. Law of Mass Action.

In treating chemical dynamics two principles of division may conveniently be adopted, according to the problem to be studied: we may consider separately the velocity of chemical changes, and the state of equilibrium reached when the change is over; or, according to the chemical systems dealt with, we may consider first equilibrium and velocity of changes in a homogeneous substance and then in a heterogeneous group of substances. Further, the phenomena may be studied either empirically from the observations or in the light of thermodynamic reasoning.

In the present chapter we shall deal only with homogeneous systems, leaving the more complex case to the next chapter; and shall defer thermodynamic treatment of either till chap. vi, using for the present only directly observed results, with occasional aid from the conceptions of the molecular theory.

A system is said to be homogeneous when ordinary observation does not show it to consist of disparate parts. Thus any mixture of gases is homogeneous—its physical properties, such as density, transparency, smell, extend to the minutest fraction that can be mechanically detached. It is only by chemical processes that it can be shown to contain different substances. So too with a solution or mixture of liquids. Chemical reactions can therefore occur within a homogeneous system consisting of mixed gases or mixed liquids. Solids do not, under ordinary circumstances, unite to form a homogeneous mixture.

Reactions sometimes occur which apparently lead to the total disappearance of some reagents present in the mixture, and appearance of others in their stead. Thus, if oxygen and hydrogen be mixed in the right proportions, and raised to a moderately high temperature, they are completely and irreversibly converted into steam. But that is not the most usual or most general case. In general reactions are *reversible*, leading to a certain state of equilibrium in which all the reagents concerned are present. Thus, in the formation of hydriodic acid at moderate temperatures,

$$H_2 + I_2 = 2\,HI.$$

When equilibrium is reached it is found that both hydriodic acid gas and the uncombined elementary gases are present. mixed; and further, that the same state of equilibrium is reached whether we start from a mixture of H_2 and I_2 or from pure HI, provided the temperature and pressure of the systems be the same, and a sufficient time is allowed for equilibrium to be reached. Such a reaction is called reversible, and is expressed by a modification of the sign of equality, thus:—

$$H_2 + I_2 \rightleftarrows 2\,HI.$$

It is not certain that any reactions are really irreversible: thus, in the case quoted previously, it is possible that a little of the oxygen and hydrogen remains uncombined. even at the lowest temperatures, as certainly some does at high. In any case apparently irreversible reactions may be treated as if they were reversible, only with the reagents on one side of the equation prevailing enormously over those on the other. Thus the laws of reversible reactions may be looked upon as general, and including those of irreversible reactions as particular cases.

The most important result that has been arrived at, with regard to equilibrium in a homogeneous system, is the *law of mass action*, frequently known by the name of Guldberg and Waage's law. This law, which was stated and proved in the preceding chapter, for perfect gases, may be considered also from the point of view of the molecular theory, and as that theory deals with the actual structure of chemical systems, a more intelligent insight into the cause and meaning of the law may thus be obtained than is possible by means of thermodynamic reasoning only. The most essential point in the molecular conception of a gas is that the independent moving particles (molecules) composing the gas are assumed to be so far apart that for the most part they do not appreciably affect one another; mutual action of the molecules only takes place in the brief time occupied in a collision between them. On this view it is easy to follow out in a general way the effect of changes in concentration of reacting gases. Thus, to take the simplest case first, suppose we have a mixture in equal volumes of hydrogen and chlorine. A certain number of collisions in which a hydrogen molecule strikes one of chlorine will occur in a second; and in some of these collisions combination will take place. Now let the concentration of the hydrogen be doubled, so that there are twice as many hydrogen molecules in a given volume; then twice as many will collide with a chlorine molecule per second, and twice as much hydrochloric acid will be formed. If the concentration of the chlorine be doubled the same effect will be produced, so that if both concentrations are doubled, say by compressing the gaseous mixture into half the volume, then four times as many collisions will occur in unit volume in unit time, and the *velocity* of reaction (i. e. quantity of combination per second) will be quadrupled. Here the action is not complicated by any appreciable reverse reaction, as hydrochloric acid gas does not dissociate noticeably at moderate temperatures. Next suppose two molecules of the same kind are required to effect the reaction, as in the formation of water. Then the rate of combination will be proportional to the number of collisions in which the required two molecules of hydrogen and one of oxygen meet; and this number will be quadrupled by doubling the concentration of the hydrogen, while it is only doubled by doubling the concentration of the oxygen. Generally we may say that if we have a reaction in which

$$\nu_A A + \nu_B B + \dots$$

combine to form new substances, the velocity of the reaction will be

$$kC_A^{\nu_A} \times C_B^{\nu_B} \dots,$$

where k is a constant.

Next suppose the reaction to be reversible, e. g. the combination of hydrogen with iodine vapour. Then collision of a hydrogen with an iodine molecule will sometimes (according to the speed of the colliding molecules and other circumstances) lead to combination; but collision of two molecules of hydriodic acid will sometimes lead to the decomposing into the elements again. Among the large number of molecules both processes will be continually taking place, and the state of equilibrium eventually arrived at means nothing more than that the composition and decomposition of HI occur at the same rate. If then we write the equation to a reaction between gases

$$\nu_A A + \nu_B B + \dots \rightleftarrows \nu_M M + \nu_N N + \dots,$$

the velocity of conversion of the left-hand system into the right is

$$kC_A^{\nu_A} \times C_B^{\nu_B} \dots;$$

that for conversion of the right-hand system into the left is

$$k'C_M^{\nu_M} \times C_N^{\nu_N} \dots,$$

and for equilibrium

$$kC_A^{\nu A} \times C_B^{\nu B} \ldots = k'C_M^{\nu M} \times C_N^{\nu N} \ldots,$$

or

$$\frac{C_M^{\nu M} \times C_N^{\nu N} \times \ldots}{C_A^{\nu A} \times C_B^{\nu B} \times \ldots} = \frac{k}{k'} = K.$$

This is Guldberg and Waage's law, as stated in chap. iii, only here we see that the reaction constant K may be regarded as the ratio between the two velocity constants k, k'.

§ 2. Chemical Equilibrium: Gases.

The number of gaseous reactions that have been studied is small, partly because not many such reactions which are reversible and take place at conveniently attainable temperatures are known, and partly because the experimental difficulties are considerable. It may be noted here that the methods available for the quantitative study of a chemical reaction fall into two groups: (1) chemical analysis, (2) measurement of some physical constant. The first of these methods is not in general applicable, as it consists essentially in removing some one or more components of the mixture to be analyzed in order to weigh; but the removal of any component alters the system and tends to set up a new state of equilibrium. E. g. suppose it were desired to find to what extent hydrogen and iodine combine at 440°; this could not be done by removing the hydriodic acid formed at that temperature, because then the state of equilibrium arrived at would be upset, and more hydrogen and iodine would combine till by repeated removal of the products all was converted into hydriodic acid. If, however, the reaction is very slow, it may be possible to carry out the analysis before sufficient time has elapsed to allow of an appreciable change in the equilibrium, especially if the reacting system can be cooled before analysis, since all reactions go on more slowly at low temperatures. Otherwise recourse must be had to the measurement of some physical constant of the unaltered mixture of reagents.

The simplest class of reversible reactions is that of *dissociation*, in which a single molecule breaks up into two or more. The well-known case of nitrogen tetroxide,

$$N_2O_4 \rightleftarrows 2NO_2$$

has been fully worked out by Natanson[1], who measured the density of the partly dissociated gas under varying pressures by a direct process similar to Regnault's method for gas densities. Applying the law of mass action to this case, we have

$$\frac{C^2_{NO_2}}{C_{N_2O_4}} = K,$$

where C_{NO_2} is the concentration of the NO_2 present (gm. mol./c.c.), and $C_{N_2O_4}$ that of the N_2O_4. A series taken from Natanson's experiments is given on p. 50; as may be seen from that, the values of K found from determinations at pressures varying from 60 to 600 mm. are satisfactorily constant.

Next, we may consider the typical and often-quoted reaction between gaseous hydrogen and iodine,

$$H_2 + I_2 \rightleftarrows 2HI,$$

studied by Hautefeuille, Lemoine, and very fully by Bodenstein[2]. The law of mass action takes the form

$$\frac{C_{H_2} \times C_{I_2}}{C^2_{HI}} = K.$$

The method adopted by Bodenstein was as follows:—A number of glass bulbs, each of about 15 c.c., were filled with pure hydriodic acid gas at the atmospheric temperature and a pressure of $\frac{1}{2}$, 1, $1\frac{1}{2}$, or 2 atmospheres. The bulbs were then sealed off and heated for a measured time by means of baths at a known temperature, varying from that of steam (100^c) to vapour of pentasulphide of phosphorus (518^c). The bulbs were then rapidly cooled and their capillary points opened under caustic potash solution; the solution dissolved the hydriodic acid remaining, as well as the iodine liberated, leaving the hydrogen. The bulb was weighed with the caustic potash contained; next filled completely with potash and weighed, and finally emptied, dried, and weighed. In this way Bodenstein determined (1) the volume of the bulbs, and hence the weight of hydriodic acid originally contained in them; (2) the volume of hydrogen liberated, and hence the weight of hydriodic acid decomposed. In a second series of experiments the bulbs were filled with a measured amount of hydrogen and a weighed amount of iodine to begin with, and treated in the same manner as before. The results of experiments made in vapour of sulphur (448^c) are shown in Fig. 23. The abscissae represent the duration of the experiment, ordinates the fraction of hydriodic acid remaining. The upper curve shows how, when all the gas originally present is HI, decomposition goes on at first rapidly, then more and more slowly, till in about two hours the state of equilibrium is reached, in which about 22 per cent. of the HI is decomposed; the lower curve shows the combination that takes place when free H_2 and I_2 are present to start with, and the same state of equilibrium reached in about the same time.

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[1] Natanson, *Wied. Ann.* 24. 465; 27. 613.

[2] Bodenstein, *Ostw.* 13. 56; 22. 1.

According to the equation $C_{H_2} \times C_{I_2} \div C^2_{HI} = K$ pressure should be without influence on the equilibrium of hydriodic acid; for if the concentration of the gaseous mixture be doubled, both numerator and denominator on the left-hand side will be increased fourfold and the value of K remains unaltered. This is generally true of reactions in

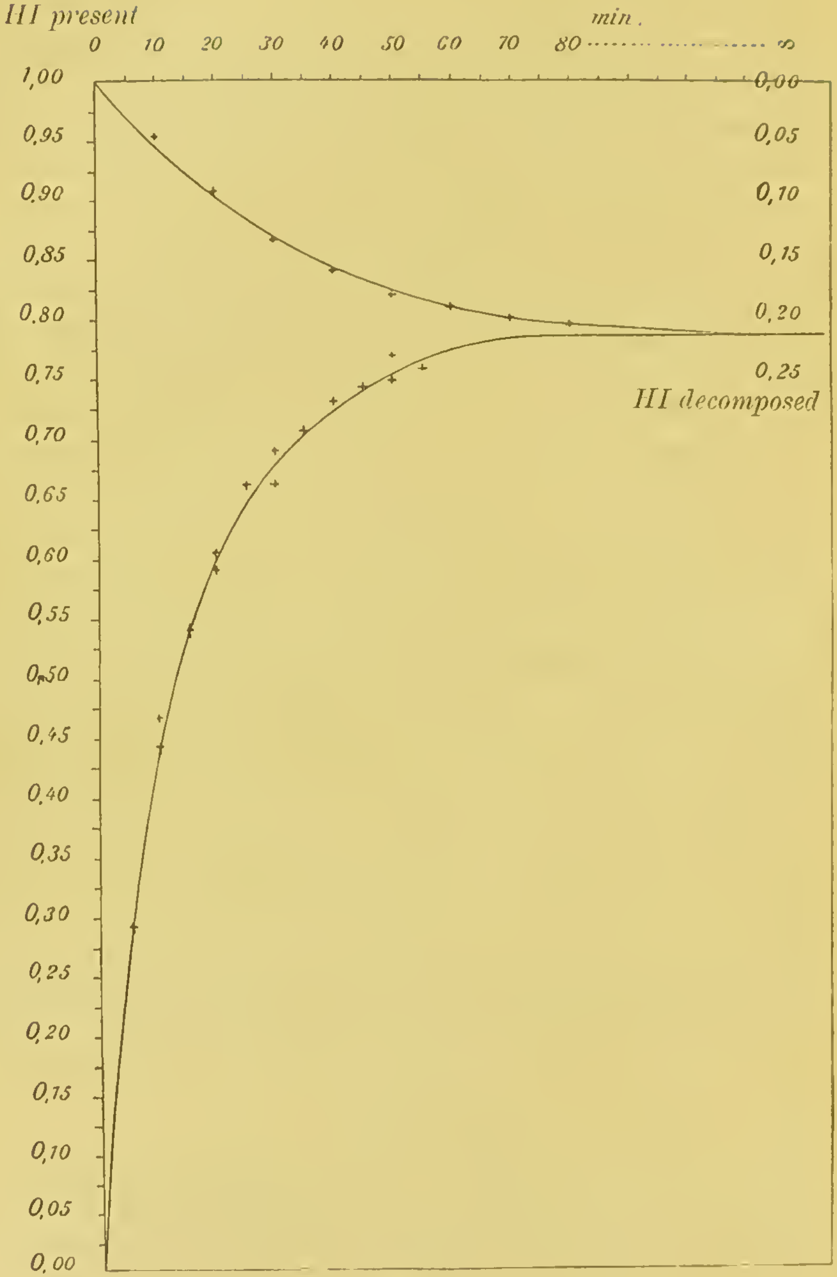
HI present
min.
0
10
20
30
40
50
60
70
80
∞
1,00
0,95
0,90
0,85
0,80
0,75
0,70
0,65
0,60
0,55
0,50
0,45
0,40
0,35
0,30
0,25
0,20
0,15
0,10
0,05
0,00
0,00
0,05
0,10
0,15
0,20
0,25
HI decomposed

Fig. 23.

which the total number of molecules formed is equal to the total number destroyed, and was directly verified by Bodenstein, who found at 448°

Original pressure of HI	$\frac{1}{2}$	1	$1\frac{1}{2}$	2 atmos.
Fraction decomposed	0·2019	0·2143	0·2225	0·2306

The agreement of these numbers is only moderately good, but would be better if it were possible to allow for a certain absorption of HI by the glass of the bulbs.

From these numbers we may calculate the reaction constant: let C be the original concentration of hydriodic acid in an experiment in which that gas alone is present to start with, and let γ be the degree of its dissociation when equilibrium is obtained, we then have present $C(1-\gamma)$ of HI, γC of H_2, and γC of I_2, so that

$$\frac{\gamma C \times \gamma C}{\{C(1-\gamma)\}^2} = \frac{\gamma^2}{(1-\gamma)^2} = K,$$

and with $\gamma = 0·2198$ $K = 0·01984$ (at 448°).

Now if hydrogen and iodine not in molecular proportions react together, the law of mass action will enable us to calculate the amount of HI formed, by means of the above value of K. Thus if one molecule of H_2 react with a molecules of I_2, and γ be the amount of free hydrogen remaining, we have $C_{H_2} = \gamma$, $C_{I_2} = a-1+\gamma$, $C_{HI} = 2(1-\gamma)$; wherefore

$$\frac{\gamma(a-1+\gamma)}{4(1-\gamma)^2} = 0·01984.$$

From this equation γ may be calculated, and the quantity of HI $= 2(1-\gamma)$ compared with that found by experiment. Bodenstein found

H_2 c.c.	I_2 c.c.	$a = \frac{I_2}{H_2}$.	HI *calc.* c.c.	HI *obs.* c.c.
20·57	5·22	0·254	10·19	10·22
20·53	25·42	1·238	34·96	34·72
19·99	100·98	5·048	39·22	39·62

The gases are measured at 0° and 760 mm., and the weight of iodine reduced to the volume it would occupy if gaseous under those conditions.

§ 3. Equilibrium in Liquids.

The conclusions arrived at as to equilibrium in gases may be extended to dilute solutions without change, since, as pointed out by van 't Hoff and others, the dissolved substances when dilute behave as if their molecules were free from mutual action, like those of a gas. It is found experimentally, however, that the law of mass action is not only true for dilute solutions, but frequently for liquid systems without restriction of concentration. The best known instance of its application to liquid mixtures is in the formation of esters, e. g.

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

This reaction proceeds so slowly that the method of chemical analysis is available ; the course of the reaction can be followed by removing a specimen at intervals and titrating the acid contained.

The law of mass action indicates that

$$\frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acid}} \times C_{\text{alcohol}}} = K\,;$$

and here, as in the preceding case, the volume occupied by the mixture does not come into consideration, since if all the concentrations are changed in the same ratio, the value of K remains the same.

If the molecular quantities of acid and alcohol be mixed, it is found that two-thirds of each are converted before equilibrium is reached, so that calling C the original concentration of each, we have

$$K = \frac{\frac{2}{3}C \times \frac{2}{3}C}{\frac{1}{3}C \times \frac{1}{3}C} = 4.$$

If, next, one molecule of acid react with a molecules of alcohol, and γ be the quantity of acid converted, then in the equilibrium condition the concentrations of the reagents are acid $1-\gamma$, alcohol $a-\gamma$, water and ester each γ, whence

$$\frac{\gamma^2}{(1-\gamma)(a-\gamma)} = K = 4,$$

and solving we get

$$\gamma = \tfrac{2}{3}\left(a+1-\sqrt{a^2-a+1}\right).$$

This equation represents very well the results of experiment, as may be seen from the following table of observations by Berthelot and Péan de St. Gilles:—

a.	γ (*obs.*).	γ (*calc.*).
0·05	0·05	0·049
0·08	0·078	0·078
0·18	0·171	0·171
0·28	0·226	0·232
0·33	0·293	0·311
0·5	0·414	0·423
0·67	0·519	0·528
1·	0·665	0·667
1·5	0·819	0·785
2·	0·858	0·845
2·24	0·876	0·864
8	0·966	0·945

Here, Guldberg and Waage's law is true, although, far from the solution being dilute, the reagents occupy the entire volume of the liquid.

When one of the reagents is present in immensely greater quantity than the others, its concentration is practically unaltered by the reaction. This is the case with the solvent in a dilute solution, if the solvent takes part in the reaction. Thus, in the preceding example, if alcohol and acid, instead of acting on one another in the pure state, are each dissolved in much water and then mixed, the small amount of water formed in the esterification will make no sensible difference to the concentration of the water. Thus in the equation

$$\frac{C_{\text{ester}} \times C_{\text{water}}}{C_{\text{acid}} \times C_{\text{alcohol}}} = K,$$

the factor C_{water}, being constant, may be transferred to the right-hand side, and the law of mass action takes the form

$$\frac{C_{\text{ester}}}{C_{\text{acid}} \times C_{\text{alcohol}}} = K',$$

and K' is often treated as the reaction constant.

More often the solvent does not take part in the reaction, and then it need not be taken into account, the dissolved substances being treated as if in the gaseous state.

We have seen in chap. i that in all electrolytic solutions the dissolved substance may be regarded as dissociating into atomic groups called ions ; these differ from ordinary products of dissociation only in being associated with positive and negative electric charges, and accordingly the law of mass action may be applied to them. In the case of weak electrolytes, organic acids, and weak bases like ammonia, the law is strictly verified, and the dissociation constant may be measured (see dichloracetic acid, p. 68). There the reaction is

$$\mathrm{CH\,Cl_2\,COOH} \rightleftarrows \mathrm{CH\,Cl_2\,COO'} + \mathrm{H^{\cdot}}\ ;$$

the positive ion is indicated by a ($^{\cdot}$), the negative by a ($'$), following the convenient usage of Ostwald. Guldberg and Waage's law indicates that

$$\frac{C_{\mathrm{CH\,Cl_2\,COO}} \times C_{\mathrm{H}}}{C_{\mathrm{CH\,Cl_2\,COOH}}} = K,$$

and measurements of electric conductivity show this to be the case. If an electrolyte break up into more than two ions, the dissociation usually takes place by stages ; thus, e.g.

$$\mathrm{H_2\,SO_4} \rightleftarrows \mathrm{HSO'_4} + \mathrm{H^{\cdot}},$$

and

$$\mathrm{H^{\cdot}} + \mathrm{HSO'_4} \rightleftarrows \mathrm{SO''_4} + \mathrm{H^{\cdot}} + \mathrm{H^{\cdot}}\ ;$$

each reaction having its own equilibrium condition.

The law of mass action, however, does not seem to apply to the dissociation of salts and strong acids and bases, in other words, strongly dissociated electrolytes. Of these an example (K Cl) was given on p. 67. It is found that instead of

$$\frac{C_{\mathrm{K}}\,C_{\mathrm{Cl}}}{C_{\mathrm{KCl}}} = \text{constant},$$

or, since the two ions are necessarily equal in amount,

$$C^2_{\text{ion}} \div C_{\text{salt}} = \text{constant},$$

the purely empirical relation

$$C^3_{\text{ion}} \div C^2_{\text{salt}} = \text{constant},$$

introduced by Rudolphi and van 't Hoff, holds approximately.

Measurements of the degree of dissociation of electrolytes may be made by several other methods as well as that of electric conductivity. The physical constants of the solution, such as the freezing point (p. 55) and the density (vid. inf.), may be made use of for the purpose; and information may be derived from the *catalytic* effect the solution has on the velocity of certain reactions, such as the inversion of cane-sugar. When the degree of dissociation is known, it can be employed in the solution of more complex problems of equilibrium in which the electrolyte takes part. Some important instances of that will be considered next.

When two electrolytes containing a common ion are mixed, the equilibrium between them can be calculated by means of the dissociation of each electrolyte separately. As an example, we will take the equilibrium between acetic acid and sodium acetate as studied by Arrhenius[1].

The method adopted was a catalytic one: the rate of inversion of cane-sugar in aqueous solution is found to depend on the acidity of the solution, and is in fact a measure of the free H-ions present. Now the rate of inversion of sugar at 54·°3 by $\frac{1}{80}$ normal H Cl has been found,

$$k = 4{\cdot}69 \times 10^{-3} \text{ per minute},$$

i. e. $4{\cdot}69 \times 10^{-3}$ of the sugar present is inverted in one minute by H Cl of the strength stated, and at that degree of dilution hydrochloric acid is practically completely dissociated.

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[1] *Ostw.* 5. 6.

The dissociation of acetic acid may be calculated from the equation $C^2_{\text{ion}} \div C_{\text{salt}} = 1{\cdot}615 \times 10^{-8}$ (concentration in gram-molecules per c.c.), and for quarter-normal acid is 0·008. Hence, if the rate of inversion is proportional to the quantity of H-ions present, it should be

$$k = 4{\cdot}69 \times 10^{-3} \times \frac{0{\cdot}008 \times \frac{1}{4}}{\frac{1}{80}} = 0{\cdot}75 \times 10^{-3}$$

for quarter-normal $C_2H_4O_2$. This is precisely the number Arrhenius found experimentally.

If now acetic acid of that strength be mixed with a small amount of sodium acetate of concentration n, the quantity of acetyl ions present is increased by the amount dissociated from the sodium acetate, and which may be approximately calculated from the relative molecular conductivity $\frac{\Lambda}{\Lambda_\infty}$. We have then equilibrium between hydrogen ions of concentration C_{H}, acetyl ions of concentration $C_{\text{H}} + \frac{n\Lambda}{\Lambda_\infty}$, and undissociated acetic acid of concentration $\frac{1}{4000} - C_{\text{H}}$, so that

$$\frac{C_{\text{H}}\left(\frac{n\Lambda}{\Lambda_\infty} + C_{\text{H}}\right)}{\frac{1}{4000} - C_{\text{H}}} = 1{\cdot}615 \times 10^{-8};$$

from this equation the value of C_{H} may be calculated, and consequently the rate of inversion. The results of Arrhenius' experiments are in good agreement with the numbers so calculated, as the following table shows:—

	$\frac{\Lambda}{\Lambda_\infty}$.	10^3k (*obs.*).	10^3k (*calc.*).
$\frac{1}{4}$ norm. $C_2H_4O_2$		0·75	0·75
,, + $\frac{1}{80}$ norm. $C_2H_3NaO_2$	0·912	0·122	0·128
,, $\frac{1}{40}$,,	0·76	0·070	0·079
,, $\frac{1}{20}$,,	0·739	0·040	0·040
,, $\frac{1}{8}$,,	0·713	0·019	0·017
,, $\frac{1}{4}$,,	0·692	0·0105	0·0088

It will be noticed that the presence of a very small amount of the salt is sufficient to reduce the dissociation of the acid to one-sixth of its amount: this is due to the much greater degree of dissociation of the salt itself.

§ 4. Avidity.

The calculation in the above case is doubtful on one point, for as sodium acetate does not follow the usual law of dissociation (Ostwald's law), its degree of dissociation must be calculated from its conductivity. But the dissociation so calculated is that it would possess when in solution alone; when mixed with acetic acid its equilibrium is slightly displaced, and the concentration of the acetyl ions is accordingly not given quite accurately by the method adopted above. The problem of equilibrium can, however, be more completely solved in the case of two weak acids, each of which follows Ostwald's law of dissociation, and whose dissociation constants are known.

Let the two acids Z_1H, Z_2H be mixed with a quantity of base MOH, insufficient to neutralize them completely, and let K_1, K_2 be their dissociation constants. Then the law of mass action yields the equations

$$\frac{C_{Z_1} \times C_H}{C_{Z_1H}} = K_1, \qquad \frac{C_{Z_2} \times C_H}{C_{Z_2H}} = K_2.$$

Now the uncombined (weak) acids, in presence of their own salts, will hardly be dissociated at all, as in the case of acetic acid and sodium acetate, so that C_H may be neglected in comparison with the concentration of the undissociated acids, C_{Z_1H}, C_{Z_2H}, and the latter quantities may be taken as expressing the amounts of uncombined acid dissociated or not. Again, the salts are almost entirely dissociated, so that the concentrations of the undissociated parts, Z_1M, Z_2M, may be neglected in comparison with the dissociated, and C_{Z_1}, C_{Z_2} practically express the amounts of the two salts.

Hence, dividing the first of the above equations by the second, we get

$$\frac{K_1}{K_2} = \frac{C_{Z_1} \times C_{Z_2H}}{C_{Z_2} \times C_{Z_1H}} = \frac{\text{salt } Z_1M \times \text{acid } Z_2H}{\text{salt } Z_2M \times \text{acid } Z_1H}.$$

If the concentration of the total base and total acids are each unity, and γ be the amount of the first acid neutralized, $1-\gamma$ is the amount of the second acid neutralized, $1-\gamma$ of the first remains free, and γ of the second. Hence

$$\frac{K_1}{K_2} = \frac{\gamma \times \gamma}{(1-\gamma)(1-\gamma)} \quad \text{or} \quad \frac{\gamma}{1-\gamma} = \sqrt{\frac{K_1}{K_2}}.$$

We see then that the equilibrium is governed by the relation between the dissociation constants of the two acids. If we write the reaction

$$Z_2M + Z_1H \rightleftarrows Z_1M + Z_2H,$$

we see that this is a reversible reaction on which it is *not necessary to make special measurements to determine the reaction constant,* since that constant is equal to $\frac{K_1}{K_2}$.

The ratio $\frac{\gamma}{(1-\gamma)}$ expresses the ratio in which the base shares itself between the two acids, and is called their relative *avidity. The relative avidity of two weak acids is therefore equal to the square root of the ratio of their dissociation constants.* The same rule holds for bases which follow the law of dissociation when in presence of acid insufficient to neutralize them completely. Ostwald's measurements of the relative avidity afford an excellent example of the use of a physical method to determine equilibrium: the method adopted was to measure the density of the solutions in order to determine how much of each of two salts was formed. The example refers to equilibrium between nitric and dichloracetic acids, a case in which the method of electric conductivities is unavailable, since nitric acid does not follow the ordinary law of dissociation, and consequently does not possess a dissociation constant[1].

1 kg. solution containing 1 gm. mol. KOH occupies at 25°	950·668	c.c.
,, ,, ,, HNO_3 ,,	966·623	,,
Sum .	1917·291	,,
Volume after mixing	1937·337	,,
Expansion	20·046	,,

1 kg. solution containing 1 gm. mol. KOH occupies at 25°	950·668	c.c.
,, ,, ,, $CHCl_2COOH$,,	947·377	,,
Sum .	1898·045	,,
Volume after mixing	1910·991	,,
Expansion	12·946	,,

Hence, if on adding nitric acid to potassium dichloracetate the latter were completely converted into nitrate, the volume would increase by $20{\cdot}046 - 12{\cdot}946 = 7{\cdot}100$ c.c. Actually, the following numbers are found :—

2 kg. solution containing 1 gm. mol. $CHCl_2COOK$ occupy	1910·991	c.c.
1 k. ,, ,, HNO_3 ,,	966·623	,,
Sum .	2877·614	,,
Volume after mixing	2883·275	,,
Expansion	5·661	,,

Hence we may conclude that $5{\cdot}661 \div 7{\cdot}100 = 0{\cdot}80$ of the dichloracetate is decomposed, and the relative avidity is

$$HNO_3 : CHCl_2COOH = 0{\cdot}80 : 0{\cdot}20 = 4 : 1.$$

Measurements of avidity can be made in a similar manner with the aid of any appropriate physical constant. A good example is to be found in the measurements of Jellet[2] on the partition of hydrochloric acid between alkaloids made long before the electrolytic dissociation theory was suggested. The alkaloids used were quinine, codein, and brucine, and the measurements were made by means of the angle of rotation of polarized light. The reaction constant in the equation

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[1] *J. f. prakt. Chem.* 18. 340.

[2] Jellet, *Trans. Irish Acad.* 25. 371 (1875).

$$\text{Quinine} + \text{Codein HCl} \rightleftarrows \text{Codein} + \text{Quinine HCl}$$

was found to be 2·03, i. e. quinine and codein, in equivalent proportions, would share HCl between them in the ratio $\sqrt{2{\cdot}03} : 1$. Similarly the reaction constant between codein and brucine was 1·58, and between brucine and quinine 0·32; the product of the three $2{\cdot}03 \times 1{\cdot}58 \times 0{\cdot}32 = 1{\cdot}026$ or approximately unity. This is in agreement with the view that the reaction constant is the ratio between the dissociation constants of the two bases, for calling the dissociation constants K_{Ch}, K_{Cod}, K_{Br} respectively, it is obvious that the product

$$\frac{K_{\text{Ch}}}{K_{\text{Cod.}}} \times \frac{K_{\text{Cod.}}}{K_{\text{Br}}} \times \frac{K_{\text{Br}}}{K_{\text{Ch}}} = 1.$$

Double decompositions between salts, acids and bases, may also be studied with the aid of knowledge of their degree of dissociation, and important conclusions arrived at. The theorems involved are, however, more elaborate, and will not be discussed here; a full account of the subject is to be found in the writings of van 't Hoff[1]. It may be remarked that according to the dissociation theory the neutralization of an acid by a base consists essentially in the formation of water from its ions. When acid and base are 'strong,' i. e. highly dissociated, nothing else occurs. Thus, e. g., the reaction of nitric acid with soda is

$$\text{Na}^{\cdot} + \text{OH}' + \text{H}^{\cdot} + \text{NO}'_3 = \text{Na}^{\cdot} + \text{NO}'_3 + \text{H}_2\text{O},$$

the Na and NO_3 being in the ionic state both before and after the reaction, so that the change is in reality only that expressed by

$$\text{OH}' + \text{H}^{\cdot} = \text{H}_2\text{O}.$$

The reaction of any strong acid with any strong base is therefore essentially the same process. This view is confirmed by experience, since the heat liberated on neutralization is the same for all strong acids and bases (cf. chap. vi). When either acid or base is weak the process is more complex, for the acid or base is but slightly dissociated, while the salt is nearly completely so ; e.g. the neutralization of ammonia by acetic acid may be written

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[1] *Lectures on Theoretical Chemistry: Lectures on Double Salts.*

$$NH_4OH + CH_3COOH = NH^{\cdot}_4 + CH_3COO' + H_2O.$$

Thus in addition to the formation of water from its ions, the previous dissociation of the ammonia and acid is implied.

§ 5. Dissociation of Water.

Water itself is dissociated, to a small but appreciable extent, into the positive and negative ions, hydrogen and hydroxyl. This is evidenced by the conductivity which even the purest obtainable water possesses. Water very carefully purified, and freed from dissolved carbon dioxide and ammonia, has a conductivity of $0{\cdot}04 \times 10^{-6}$ mhos. according to Kohlrausch[1]. This number, with the aid of the ionic velocities of H and OH, gives $1{\cdot}07 \times 10^{-10}$ as its degree of dissociation, i. e. $1{\cdot}07 \times 10^{-10}$ gm. molecules exist in the ionic state, in every c.c. of water. Several important conclusions may be drawn from this as to the part played by water in certain reactions. Thus salts of weak acids and bases are to some extent dissociated *hydrolytically*, i. e. by the action of water itself as a very weak acid, or very weak base (vid. inf.). Arrhenius[2] found in that way $1{\cdot}1 \times 10^{-10}$ as the degree of dissociation. Wys[3] has in a similar manner calculated the degree of dissociation of water from the rate of esterification it produces, and finds $1{\cdot}2 \times 10^{-10}$; and Ostwald[4] obtained 1×10^{-10} at 25° as the value of the same constant by reasoning based on the electromotive force of a gas battery (chap. vii). The remarkable agreement of these numbers, all obtained by different methods, and referring to a phenomenon so much the reverse of obvious, must be regarded as a very strong argument for the correctness of the electrolytic dissociation theory, on which they are all based.

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[1] Kohlrausch and Heydweiller, *Ostw.* 14. 317.

[2] Arrhenius, *Ostw.* 11. 827.

[3] Wys, *Ostw.* 11. 492 ; 12. 514 : Van Laar, l. c., 13. 736.

[4] Ostwald, *Ostw.* 11. 521 ; Bredig, l. c., 11. 829.

§ 6. **Hydrolysis.**

Water is capable of acting either as a weak acid, or a weak base. E. g. suppose hydrochloric acid be added to neutralize a very weak base, such as urea, in aqueous solution: then the acid will divide itself between the urea and the water, just as it might divide between two other bases of comparable strength, such as ammonia and methylamine. Writing *M* for the base, we have to do with the reaction

$$MCl + H_2O \rightleftarrows HCl + MOH,$$

or in terms of the electrolytic theory, if the salt be nearly completely dissociated, but the weak base hardly at all,

$$M^{\cdot} + Cl' + H_2O \rightleftarrows H^{\cdot} + Cl' + MOH,$$

or simply

$$M^{\cdot} + H_2O \rightleftarrows H^{\cdot} + MOH.$$

Applying the law of mass action to this case, we have

$$\frac{C_{H} \times C_{MOH}}{C_{M}} = \text{const.},$$

the factor C_{H_2O} being left out of the equation, since water is present in practically unlimited quantity and its concentration may therefore be regarded as constant. This conclusion was verified experimentally by Walker, who treated normal hydrochloric acid with varying amounts of urea, and determined the quantity of hydrogen ions remaining in solution by the rate of inversion of cane-sugar.

We may, however, learn more by taking the dissociation of water explicitly into account. That dissociation is expressed by

$$H_2O \rightleftarrows H^{\cdot} + OH',$$

and accordingly should be calculable by means of an equation

$$\frac{C_H \times C_{OH}}{C_{H_2O}} = K,$$

in which K is the dissociation constant of water. If, as in the section on avidity, we compare this formula with the corresponding one for a weak base

$$\frac{C_M \times C_{OH}}{C_{MOH}} = K',$$

we get

$$\frac{C_H \times C_{MOH}}{C_M \times C_{H_2O}} = \frac{K}{K'} \quad \text{or} \quad \frac{C_H \times C_{MOH}}{C_M} = \frac{K}{K'} \times C_{H_2O}$$

identical with the equation previously found for hydrolysis, only that we now have the means of calculating the reaction constant.

Precisely similar relations hold in the case of a salt formed by a strong base and a weak acid (ZH), leading to the result that

$$\frac{C_{OH} \times C_{ZH}}{C_Z} = \frac{K}{K''} \times C_{H_2O},$$

where K'' is the dissociation constant of the acid. It is in this way that the value of K has been calculated from experimental data by Shields[1]. Thus a 0·0952 normal solution of sodium acetate is hydrolyzed to the extent of 0·008 per cent. at 24°·2, so that

$$C_{OH} = C_{CH_3COOH} = 0{\cdot}00008 \times 0{\cdot}0000952 \text{ (gm. mol./c.c.)},$$

$$C_{CH_3COO} = (1 - 0{\cdot}00008) \times 0{\cdot}0000952.$$

To be quite systematic, the concentration of water ought to be taken as $\frac{1}{18}$ (gm. mol. per c.c.), but it is usually taken as unity, or in other words, ignored altogether, in the equation of Guldberg and Waage's law. Accordingly the reaction constant for hydrolysis of sodium acetate is

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[1] *Ostw.* 12. 184.

$$\frac{C_{\mathrm{OH}} \times C_{\mathrm{ZH}}}{C_{\mathrm{Z}}} = 0{\cdot}61 \times 10^{-12} = \frac{K}{K''}.$$

But K'', the dissociation constant of acetic acid at $25°, = 1{\cdot}81 \times 10^{-5}$, whence

$$K = 1{\cdot}1 \times 10^{-10}.$$

Now, since $C_{\mathrm{H}} = C_{\mathrm{OH}}$ and $C_{\mathrm{H_2O}}$ is assumed to be unity, it follows that $\sqrt{K} = 1{\cdot}05 \times 10^{-10}$ is the concentration of the hydrogen or hydroxyl ions in pure water at 25°.

The phenomenon of hydrolysis is more marked when acid and base forming the salt to be hydrolyzed are both weak, but in that case a different equation holds good. Here we must assume that both acid and base are but slightly dissociated, while the salt is nearly completely so. We get accordingly the reaction

$$\mathrm{MZ} + \mathrm{H_2O} \rightleftarrows \mathrm{MOH} + \mathrm{ZH}$$

practically in the form

$$\mathrm{M}^{\cdot} + \mathrm{Z}' + \mathrm{H_2O} \rightleftarrows \mathrm{MOH} + \mathrm{ZH},$$

and the law of mass action is expressed by

$$\frac{C_{\mathrm{MOH}} \times C_{\mathrm{ZH}}}{C_{\mathrm{M}} \times C_{\mathrm{Z}}} = \frac{C_{\mathrm{MOH}} \times C_{\mathrm{ZH}}}{C^2_{\mathrm{salt}}} = \text{const.}$$

So that if the total concentration of each reagent is doubled, the numerator and denominator of the fraction are each quadrupled, and equilibrium still holds: or, in other words, the degree of hydrolysis is independent of the concentration. This conclusion is approximately confirmed by the experiments of Arrhenius and Walker on the hydrolysis of aniline acetate[1].

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[1] *Ostw.* 5. 18.

§ 7. Influence of Temperature on Equilibrium.

Since the state of equilibrium existing at any one temperature can be expressed by a single quantity—the reaction constant—the effect of change of temperature can only be to change the value of that quantity. The problem then is to find the variation of the reaction constant—K—with temperature; the variation is, as shown at the end of the last chapter, intimately connected with the heat of reaction. The connexion will be dealt with in detail in chap. vi; here we may be content with some experimental data, and with such light as reasoning based on the kinetic theory throws on them.

Equilibrium in a dissociating gas is regarded as being the result of two processes: the decomposition of some molecules, and the recombination of the dissociated parts. The former may be, and probably is, in most cases a spontaneous breaking up of a molecule in consequence of the relative motion of the atoms composing it, although in some cases the breaking up may be brought about by collision with another molecule. But the reserve process can, obviously, only take place when the combining parts come within one another's range of action. Now rise of temperature means increased average velocity of the molecules, and since by repeated collisions a repeated interchange occurs between the various forms of energy in the molecule, the relative velocities of its parts will be increased too, so that there will be a greater chance of the attractive forces between the atoms being overcome, and the molecule flying to pieces. On the other hand, there will be an increased number of collisions between the dissociated parts of the molecules, offering opportunities for recombination; but this will be compensated by the fact that, as the colliding parts are moving more rapidly, they are more likely to fly past one another's range of action, and so avoid recombination.

Thus, on the whole, the effect of rise of temperature is to increase the degree of dissociation. This is regularly observed to be the case. Thus the table quoted on p. 50 shows that at 21·5° N_2O_4 is only dissociated to the extent $\gamma = 0{\cdot}174$ at a pressure approaching that of the atmosphere: but at 130°, under atmospheric pressure the density of the gas is that of NO_2, showing that the dissociation is practically complete. Two observations of Deville and Troost on the same gas at atmospheric pressure give

	Specific gravity.	*Degree of dissociation.* γ
26·7° C.	2·65	0·1996
111·3°	1·65	0 9267

Again, sulphur vapour is progressively dissociated on rise of temperature. The phenomenon here is not so simple, and it has been suggested[1] that three kinds of molecules occur in the vapour—S_8, S_6, and S_2, and that the dissociation takes place in two stages,

$$S_8 \rightleftarrows S_6 + S_2 \text{ and } S_6 \rightleftarrows 3S_2.$$

Several gases have been observed to dissociate slightly when heated to high temperatures, the most noteworthy instances being (1) iodine vapour, which consists of diatomic molecules at low temperatures, but monatomic at high; (2) carbon dioxide breaking up into carbon monoxide and oxygen; (3) steam, which dissociates into oxygen and hydrogen. These gases are quite stable at moderate temperatures, and only dissociate appreciably when near the highest temperatures practically attainable, but it is to be presumed that if they could be heated sufficiently they would be decomposed completely, like nitrogen tetroxide. The cases of steam and carbon dioxide are, however, possibly not strict dissociations; thus the reaction in the case of steam may require the interaction of two molecules, as

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[1] Riecke, *Ostw.* 6. 430.

$$2\,H_2O \rightleftarrows 2\,H_2 + O_2,$$

or it may take place by the spontaneous breaking up of one molecule,

$$H_2O \rightleftarrows H_2 + O,$$

with subsequent combination of two oxygen atoms to form a molecule. In either case the reaction is not so simple as in dissociation proper, and the argument given above as to effect of temperature cannot be applied with certainty. If now we proceed to a case in which undoubtedly two molecules are involved, the reaction

$$2\,HI = H_2 + I_2,$$

it is impossible to say beforehand whether rise of temperature will favour the decomposition or the formation of hydriodic acid. Experiment shows that[1]

Fraction of HI decomposed at	350°	0·1946
,, ,,	448°	0·2198

i. e. rise of temperature favours decomposition, but only to a small extent.

In solutions no general rule can be given, for the degree of dissociation sometimes increases, sometimes decreases with rise of temperature—doubtless the interaction between solvent and dissolved substance prevents the possibility of applying simple kinetic reasoning. Examples of this will be considered in chap. vi in connexion with the quantity of heat evolved in dissociation.

The same may be said of reactions between liquids other than solutions: amongst the best known of such reactions is the formation and decomposition of ethyl acetate (p. 163). The reaction constant here is = 4 not only at atmospheric temperature, but without appreciable change up to 220°. But no general rule can be given, for some reactions proceed further, some less far, on rise of temperature.

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[1] Bodenstein, *Ostw.* 22. 16.

§ 8. Velocity of Reaction.

For the study of velocity of reaction in homogeneous systems, the same methods are available as for determination of equilibrium; but with the difference that attention must be paid to the time during which the materials are left in contact. The problem is, however, in most cases complicated, not only by reversibility of the reaction itself, but by secondary reactions that may set in, due to the new products formed, and in some cases to action of the walls of the reaction vessel, or of the solvent. Hence the comparatively limited number of cases in which it has been found possible to trace clearly the mechanism of the process. In the sense of the law of mass action, the 'velocity' of a combination between ν_A molecules of a substance A, ν_B of B, &c., is given by

$$kC_A^{\nu A} \cdot C_B^{\nu B} \dots,$$

where k is a constant; but in general the reaction is reversible, so that if M, N, &c. be the products formed, they at once begin to suffer conversion in the inverse sense at the rate

$$k' C_M^{\nu M} \cdot C_N^{\nu N} \dots,$$

and the net rate of conversion is the difference

$$kC_A^{\nu A} \cdot C_B^{\nu B} \dots - k' C_M^{\nu M} \cdot C_N^{\nu N} \dots.$$

When this expression becomes zero in consequence of the decrease in C_A, $C_B \dots$ and increase in C_M, $C_N \dots$, equilibrium is reached. In each of these expressions the velocity of reaction is measured by the quantity converted per unit volume and per unit time, and the quantity per unit volume must be expressed in the unit adopted for C.

In many cases the converse reaction practically does not take place, and then it becomes much easier to follow the course of the change. Such cases may best be classed according to the number of molecules taking part in the reaction; we have therefore first to deal with the dissociation of a single molecule.

(*a*) *Monomolecular reaction.*

Here there is only one concentration to consider: the velocity is expressed simply by kC, and since the velocity means the rate at which the substance is dissociated, we may say that

$$\left[-\frac{dC}{dt} = kC, \quad \text{or in words}\right]$$

the rate at which the dissociation takes place is constantly proportional to the concentration of the dissociating substance present; as the latter falls off in consequence of the progress of the reaction, the velocity falls off too.

An example of such a reaction (in gaseous form) is to be found in the decomposition of arsine. This takes place simply according to the equation

$$AsH_3 = As + 3H,$$

and the subsequent combination of the hydrogen atoms to form molecules has no influence on the primary reaction. The reaction has been studied quantitatively[1] by enclosing arsine at atmospheric pressure in a glass bulb closed by a capillary, through which it is connected to a mercury manometer. The bulb is heated, e.g. in a bath of diphenylamine vapour (310°), for several hours, and as one molecule of arsine is replaced by one and a half molecules of hydrogen, the pressure gradually rises, and the extent of decomposition at any moment may be determined by that means. An experiment gave the following results:—

Time in hours.	*Pressure* (mm.).	$\frac{C}{C_0}$.	k.
0	784·84	1·	—
3	878·50	0·76133	0·0908
4	904·05	0·69367	914
5	928·02	0·63514	908
6	949·28	0·58097	905
7	969·08	0·53051	904
8	987·19	0·48435	906

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[1] Kooij, van 't Hoff, *Studies in Chemical Dynamics* (1896), p. 2.

The third column gives the concentration C of the arsine at the moment of observation, expressed as a fraction of the original concentration; the fourth column gives k the velocity constant, the unit of time being the hour. Thus during the first three hours the concentration fell by 0·23867, or 0·07956 per hour, but during that time its average value was

$$(1 + 0{\cdot}76133) \div 2 = 0{\cdot}88066.$$

Hence, as k is the ratio between rate of concentration and existing concentration,

$$k = 0{\cdot}07956 \div 0{\cdot}88066 = 0{\cdot}0903.$$

This reasoning is, however, not quite exact, since the concentration does not keep at the average value 0·88066, but varies continuously. The numbers in the last column of the table were actually obtained by integrating the differential equation $\frac{dC}{dt} = kC$, which yields

$$\log_e\left(\frac{C_0}{C}\right) = kt,$$

whence k may be calculated. The statement $k = 0{\cdot}0908$ may be put into words as follows:—If arsine were kept for an hour at 310°, and the amount decomposed were continually replaced by a fresh supply, so that its mass remained always the same, then 0·0908, i. e. 9·08 per cent. of the amount originally present, would be decomposed.

The decomposition of phosphine has also been studied by Kooij with similar results, so that it is to be regarded as a monomolecular reaction.

The best known monomolecular reaction among liquids is the inversion of cane-sugar, according to the equation,

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

A molecule of cane-sugar in aqueous solution combines with a molecule of water and breaks into a molecule each of the isomers dextrose and laevulose. The reaction is excessively slow in pure water, but in presence of acids becomes moderately rapid, and in any case it is practically irreversible. Cane-sugar solution rotates the plane of polarization of light right-handedly to an extent that is roughly proportional to the concentration, the mixture of dextrose and laevulose is on the whole laevo-rotatory; hence the progress of the reaction can be followed quantitatively by measurements with the polariscope. Though two molecules are involved in the inversion, one of them being water belongs to a substance present in very great excess, so that its concentration may be left out of account; we may therefore anticipate that the reaction will follow the rule for monomolecular change, viz. $\log\left(\frac{C_0}{C}\right) = kt$, and this is verified accurately by experiment; indeed the above expression was arrived at empirically before the law of mass action had been propounded. Thus, Wilhelmy found for 20 per cent. sugar solution in presence of half-normal lactic acid at 25° the following numbers:—

t (minutes).	a (angle of rotation).	$\frac{1}{t}\log_e\frac{C_0}{C} = k$.
0	34·50°	—
1435	31·10	0·0000541
4315	25·00	543
7070	20·16	539
11360	13·98	532
14170	10·61	530
16935	7·57	533
19815	5·08	528
29925	− 1·65	526

whilst the completely inverted mixture ($t = \infty$) gave $a = -10{\cdot}77$.

(b) *Bimolecular reaction.*

When two molecules, A and B, react together, and the action is irreversible, the expression $kC_A C_B$ holds for the quantity converted in unit volume and unit time; if the two molecules are of the same kind, this, of course, simplifies to kC^2.

[Calling the original concentrations C_{A_0} C_{B_0}, and the amount of either consumed per unit of volume γ (the 'degree of reaction'), we have

$$C_A = C_{A_0} - \gamma, \quad C_B = C_{B_0} - \gamma.$$

The velocity of reaction is represented by $\frac{d\gamma}{dt}$, so that we obtain the differential equation

$$-\frac{d\gamma}{dt} = k\,(C_{A_0} - \gamma)\,(C_{B_0} - \gamma),$$

or

$$\frac{-d\gamma}{(C_{A_0} - \gamma)\,(C_{B_0} - \gamma)} = k\,dt.$$

This may be solved by resolving into partial fractions, giving

$$\frac{d\gamma}{C_{A_0} - C_{B_0}}\left(\frac{1}{C_{A_0} - \gamma} - \frac{1}{C_{B_0} - \gamma}\right) = k\,dt,$$

whence on integrating

$$\frac{1}{C_{A_0} - C_{B_0}} \log \frac{C_{B_0} - \gamma}{C_{A_0} - \gamma} = kt + \text{const.};$$

but when $t = 0$, $x = 0$,

so that

$$\frac{1}{C_{A_0} - C_{B_0}} \log \frac{C_{B_0}}{C_{A_0}} = \text{const.},$$

and finally

$$k = \frac{1}{(C_{A_0} - C_{B_0})\,t} \log \frac{(C_{B_0} - \gamma)\,C_{A_0}}{(C_{A_0} - \gamma)\,C_{B_0}}.$$

But in the important particular case of $C_{A_0} = C_{B_0} = C_0$ say, this expression becomes indeterminate. We then have

$$-\frac{d\gamma}{dt} = k\,(C_0 - \gamma)^2,$$

whence

$$k = \frac{\gamma}{t\,(C_0 - \gamma)\,C_0}.$$

This equation obviously holds when the two molecules are of the same kind.]

As a typical instance of a bimolecular reaction, we may consider the saponification of the esters—a reaction that has been much used as a means of estimating the activity of bases. The reaction for ethyl acetate and soda is expressed by the equation

$$C_2H_5OOCCH_3 + Na\,OH = C_2H_5OH + CH_3COO\,Na,$$

or, in terms of the electrolytic dissociation theory, since both soda and sodium acetate may be looked upon as completely dissociated,

$$C_2H_5OOCCH_3 + OH' = C_2H_5OH + CH_3COO';$$

in either case bimolecular.

The reaction is a somewhat rapid one, but it is possible to determine its course by a simple titration of the excess of soda remaining. In order to do so with success, the specimen to be titrated must be brought under the burette only a few seconds before the moment at which its strength is desired, and the estimation completed in the shortest time possible. Solutions containing $\frac{1}{20}$ gram-molecule per litre are of convenient rapidity in action.

The majority of reactions appear to be bimolecular, but of course many of them are more or less reversible, and consequently not so simple in their course as the above example. A few instances of trimolecular reactions have been discovered and followed out quantitatively, but none in which more than three molecules take part. This is not to be wondered at when the mechanism of the reaction is borne in mind. A trimolecular reaction is one in which a simultaneous collision of three specified kinds of molecules is required to effect the rearrangement of the atoms; such collisions will clearly be very much rarer than collisions between two molecules, and accordingly the materials will much more often react in a manner that can be accomplished by ordinary dual collisions. Simultaneous collision between four or more molecules must be still rarer, so rare, indeed, as to have no practical influence on the course of chemical reactions. This reasoning is the more markedly true, the more dilute the reacting system considered, and it should be remembered that Guldberg and Waage's law, whether based upon thermodynamics, or on reasoning from the kinetic theory such as that used above, has only been proved to hold for very dilute systems, gases or solutions, although in particular cases it may be true for greater concentration; the assumptions made in the kinetic proof are that the molecules are so far apart as not to influence each other sensibly except during collision, and that the volume actually occupied by the molecules may be neglected by comparison with the whole volume, and experiment shows that these conditions are about satisfied for decinormal solutions and gases (a gram-molecule of gas at atmospheric pressure occupies about 22 litres; hence a 'decinormal gas' is at 2·2 atmospheres pressure at 0°).

(*c*) *Trimolecular reaction.*

If one molecule each of A, B and C combine, the velocity of reaction is $k\,C_A\,C_B\,C_C$; if two molecules of A combine with one of B the expression becomes $k\,C_A{}^2\,C_B$; and if all three molecules are alike, it reduces to kC^3. The course of the reaction may be calculated in a way similar to that used for the bimolecular reaction, and if the three molecules are alike, or, being different, are present in equivalent proportions at the beginning of the reaction, we arrive at the conclusion

$$k = \frac{1}{t}\cdot\frac{\gamma\,(2\,C_0-\gamma)}{2\,C_0{}^2\,(C_0-\gamma)^2},$$

where t is the time since the concentration of each reagent had the initial value C_0, and γ is the extent by which the original concentration of each has fallen off, at that time.

A reaction of this kind, studied by Noyes and Cottle[1], is the reduction of silver by sodium formate,

$$2C_2H_3O_2Ag + HCO_2Na$$
$$= 2Ag + CO_2 + C_2H_3O_2H + C_2H_3O_2\,Na.$$

The silver and sodium salts may be looked upon as completely dissociated, so that the above may be written,

$$2Ag^{\cdot} + HCOO' = 2Ag + CO_2 + H^{\cdot},$$

and subsequent combination of the hydrogen ion with the acetyl residue. It may therefore be expected to be trimolecular, and so it was actually found. A series of experiments at 100° with decinormal solutions gave

t (minutes).	C.	k (trimol.).	k (bimol.).
0	0·10000	—	—
2	·06694	30·8	2·57
4	·05334	31·3	2·19
6	·04684	29·6	1·89
9	·03784	33·3	1·83
14	·03235	30·6	1·61

The last two columns give the values of k calculated according to the tri- and bi-molecular formulae respectively. It is clear that the former only is applicable.

§ 9. Number of Reacting Molecules.

The last example is a good instance of the way in which it is possible to determine the number of molecules taking part in a reaction. It often happens, however, that secondary influences, such as the subsidiary reactions of the products formed, or in gases the influence of the walls of the containing vessel, are sufficient to obscure the somewhat narrow distinction between mono- and bi-molecular, or between bi- and tri-molecular reaction, when studied in the way already described. There is another method in which the distinction between the various kinds of reaction is more marked, viz. that of comparing the velocity for different degrees of concentration. In a monomolecular reaction the velocity is proportional to the concentration, velocity being measured by rate of decrease of the concentration itself; hence, if the volume in which a certain mass of reagent occurs is doubled, the 'velocity of reaction' is halved, but the total amount of reagent converted remains the same as before; in other words, the fraction of the whole mass converted in a second is independent of the density of the reacting substance. In a bimolecular reaction the velocity is proportional to the product of two concentrations, or to the square of one; so that if the volume be doubled, the quantity reacting per second in each cubic centimetre is reduced to one quarter, and the total amount of reaction is but half that occurring when the same mass of reagent occupies the smaller space. In the same way, the velocity of a trimolecular reaction is proportional to the cube of the concentration, and we may conclude that the percentage of the reagents converted in a given time will be (1) constant, (2) inversely proportional to the volume, (3) inversely proportional to the volume squared, according as the reaction is mono-, bi-, or trimolecular.

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[1] *Ostw.* 27. 579.

This test has been applied to the formation of cyamelide, which is a polymer of cyanic acid NCOH. The latter is a gas, and gradually suffers transformation into the solid cyamelide, at ordinary temperatures; if its volume be kept constant the pressure gradually falls, and serves as a measure of the falling concentration. The experiment[1] was made by filling with cyanic acid a small bulb, terminating below in a tube in which mercury was kept at a constant level. In 23 hours the pressure fell from 188·84 to 153·46, or at the rate of 1·538 per hour. The bulb terminated above in a tap, leading to an equal-sized vacuous bulb; this tap was now opened so as to allow the gas to double its volume.

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[1] Van 't Hoff, *Studies in Chemical Dynamics* (1896), p. 108.

Then in the course of 20 hours the pressure fell from 79·01 to 76·04, or 0·1485 per hour, or 10·4 times as slowly as before. Now the average pressure in the first part of the experiment was 2·21 times as great as that observed after opening the tap, so that if the reaction were bimolecular it should go $(2{\cdot}21)^2 = 4{\cdot}88$ times as slowly after opening the tap as before, but if trimolecular $(2{\cdot}21)^3 = 10{\cdot}7$ times as slowly. The conclusion is that three molecules take part in the reaction, and that the formula of cyamelide is $N_3C_3O_3H_3$.

In most cases the molecular formula usually adopted as expressive of the complete effect of a reaction involves a much larger number of molecules than that required to effect the principal reaction. Sometimes the molecular formula may be simplified, so as to correspond to the real process, if the electrolytic dissociation of the reagents is taken into account; more often, however, two or more reactions occur simultaneously, and the molecular formula only gives the total change, affording no insight into the steps by which it is brought about; e. g. the combustion of phosphine is usually written

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O,$$

but it is not really hexamolecular. Van der Stadt[1] showed that it is in its first stage bimolecular, and was even able to obtain the products of the primary reaction, metaphosphorous acid and hydrogen, in theoretical quantities, proving that reaction to be

$$PH_3 + O_2 = PO_2H + H_2.$$

In some other gaseous reactions the first stage of the process has been distinguished; e. g. in the combustion of acetylene[2], which as a whole runs

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O,$$

[1] *Ostw.* 12. 322.

[2] Bone and Cain, *J. C. S.* 71. 26.

the first stage is again bimolecular, viz.:—

$$C_2H_2 + O_2 = 2CO + H_2.$$

In many other cases the number of molecules taking part in the primary reaction has been determined, but it is not possible to say with certainty what that reaction is.

§ 10. Avidity Measurements by means of Velocity of Reaction.

Several reactions have been employed to determine the strength or avidity of acids and bases, i.e. the concentration of the free hydrogen or hydroxyl ions they contain. This can be most easily and satisfactorily done when the reaction is a catalytic one, taking place under the influence of the acid or base, which itself remains unchanged in quantity. The most perfect instance known of such a reaction is the inversion of cane-sugar already discussed. It is catalytic; it can be followed by a simple physical method—that of the polarimeter—which does not in any way interfere with the progress of the reaction; and its velocity is approximately proportional to the concentration of the hydrogen ions producing it. The proportionality is closest in the case of weak acids; it may be tested by a glance at the following table, which shows (1) the strength of the acid in half-normal solution, obtained by comparison of the rate of inversion with that for hydrochloric acid, the dissociation of which is practically complete; (2) the degree of dissociation as calculated from the electrolytic conductivity, both at 25° from the measurements of Ostwald:—

	Rate of inversion.	*Degree of dissociation.*	*Dissociation constant.*
Dichloracetic acid .	0·271	0·272	51×10^{-6}
Monochloracetic acid	0·0484	0·0542	$1·55 \times 10^{-6}$
Formic acid . . .	0·0153	0·0245	$0·214 \times 10^{-6}$
Acetic acid . . .	0·0040	0·0060	$0·018 \times 10^{-6}$

For acids stronger than dichloracetic it is not possible to state a dissociation constant, for they do not follow the usual law of dissociation; but for such acids the rate of inversion serves to indicate the order of their strength, although not proportional to it; e.g. the rate of inversion by HCl increases more rapidly than the concentration, although the concentration of the hydrogen ions necessarily increases less rapidly than the total concentration of HCl. Some secondary influence, due probably to the negative ion in the solution, here complicates the results.

Another reaction which has been employed for determining the strength of acids is the decomposition of esters, especially of methyl and ethyl acetates. The reaction, e.g.

$$CH_3OOCCH_3 + H_2O = CH_3OH + CH_3COOH,$$

is really a reversible one, but (p. 163) when one of the reagents is in great excess the equilibrium is driven so far in the opposite direction that it may be looked upon as irreversible. Thus if methyl acetate be taken in dilute aqueous solution, the decomposition due to mutual action between molecules of ester and molecules of water so far prevails over the recombination, that the rate of decomposition practically follows the rule for a monomolecular reaction. Like the inversion of cane-sugar, this reaction only goes with measurable velocity in presence of acids, and to a first approximation is proportional to their strength, i. e. to the concentration of the hydrogen ions they contain. The progress of the decomposition may be followed very easily by titrating the acetic acid formed.

Another reaction, studied by Ostwald in connexion with measurements of avidity, is the decomposition of acetamide by acids, e. g.

$$CH_3CONH_2 + H\,Cl + H_2O = NH_4Cl + CH_3COOH.$$

From the point of view of the electrolytic dissociation theory, this may be regarded as

$$CH_3CONH_2 + H_2O = CH_3COO' + NH_4^{\cdot},$$

and subsequent combination of the acetyl ion with hydrogen, except when the solution is so very dilute that acetic acid remains dissociated. The velocity of the reaction may most conveniently be studied by decomposing the ammonium salt formed by means of sodium hypobromite, and measuring the nitrogen evolved. Here again the velocity is not strictly proportional to the strength of the acid used, on account of the influence of the neutral salt (NH_4Cl); the salt increases the activity of the H-ions, and so makes strong acids appear stronger than they really are.

There is no reaction available for measuring the strength of bases which is so convenient and satisfactory as the inversion of cane-sugar for acids. It has been attempted to use the conversion of hyoscyamine ($C_{17}H_{23}NO_3$) into its isomer atropine[1], since that is a process which takes place catalytically under the influence of hydroxyl ions. Both alkaloids rotate polarized light, but to a different extent, so that the degree of conversion can be easily measured; unfortunately atropine suffers a further change, decomposing into tropic acid and tropine, which complicates the results and makes them of little value for estimating the concentration of the hydroxyl ions.

The reactions which have been successfully used for the purpose are not catalytic; the best known of them is the saponification of esters already referred to (p. 183). The rate of saponification by various bases has been determined by Ostwald, Reicher, and others, and the velocity constant of the reaction indicates the order of strength of the base, i. e. the concentration of the OH-ions in it; but in the case of weak bases (ammonia, allylamine) the velocity is far from proportional to the strength of the base taken by itself, for the neutral salt formed in the reaction decreases the degree of dissociation of the base enormously in a manner precisely similar to the effect on weak acids (p. 166) already discussed.

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[1] Will and Bredig, *Ber.* 21. 2777.

Another reaction, employed by van 't Hoff, is the decomposition of sodium monochloracetate,

$$CH_2Cl . COONa + NaOH = CH_2OH . COONa + NaCl,$$

which takes place under the influence of bases with formation of sodium glycollate.

In any measurements by means of the velocity of reaction especial care must be taken to maintain constancy of temperature, since, as will appear below, the velocity of reaction is influenced enormously by temperature. The temperature coefficient of velocity of reaction is commonly as much as 10 to 12 per cent. per degree, so that an error of only one-tenth of a degree in the temperature at which the reaction is carried out would involve an error of more than 1 per cent. in the result arrived at.

§ 11. Velocity in Reversible Reactions.

When the converse of a reaction takes place to a measurable extent, or in other words, when in the state of equilibrium the substances written on the left as well as on the right hand side of the equation exist in measurable quantity, there are two velocity constants instead of one to determine, and the problem of determining them becomes more complicated. Fortunately it is not necessary in practice to get a general expression for the velocity at any stage of the reaction. It is sufficient to measure (1) the initial velocity of reaction when the first set of reagents is mixed to obtain k, and (2) the initial velocity when the second set is mixed to obtain k'. For the velocity at any time is expressed by

$$kC_A^{\nu_A} . C_B^{\nu_B} \ldots - k'C_M^{\nu_M} . C_N^{\nu_N} \ldots$$

(p. 178), but if the system AB . . . be taken to start with, then for some time the quantity of MN . . . formed will be so small that the second term in the above expression may be regarded as negligible, and the reaction may be treated in the same manner as an irreversible one, and k deduced by one of the equations already given, according as one, two, or three molecules of the substances $AB\ldots$ react. Similarly by starting with $MN\ldots$ only, the quantity of $AB\ldots$ present may for some time be neglected, and we have the means of calculating k'.

A good instance of such a determination is given by van 't Hoff from the experiments of Knoblauch[1]. The reaction studied was the formation of an ester,

$$CH_3COOH + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2O.$$

In the first place, acetic acid was dissolved in a mixture (in molecular proportions) of alcohol and water, and HCl added to accelerate the reaction. This liquid contained, at 25°, the temperature at which the reaction was carried out, 1 gram-molecule of acetic acid, and 12·756 gram-molecules of alcohol per litre. The progress of the reaction was found to be

Time (minutes). t.	*Concentration of ester.* C.	*Velocity of conversion.* $\frac{dC}{dt}$.
0	0·	
44	0·1327	0·00302
53	0·1628	0·00307
62	0·1847	0·00298
70	0·2128	0·00304

The mean value of $\frac{dC}{dt} = 0{\cdot}00303$. It is clear that during this period the velocity is practically unaffected by the products formed; we may therefore set

$$\text{Velocity} = kC_{\text{acid}} \,.\, C_{\text{alcohol}},$$

or

$$0{\cdot}00303 = k \times 1 \times 12{\cdot}756,$$

whence

$$k = 0{\cdot}000238.$$

In the second place, ethyl acetate was dissolved in a mixture of alcohol and water, to which HCl was added as before. The mixturecontained 1 gram-molecule of ethyl acetate and 12·215 gram-molecules of water in one litre, and the reaction took place as follows:—

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[1] *Ostw.* 22. 268.

Time (minutes). t.	*Concentration of acid.* C.	*Velocity.* $\frac{dC}{dt}$.
0	0	
78	0·0777	0·000966
86	0·0862	0·001003
94	0·093	0·000989

the mean value of the velocity being 0·000996. But in this case the velocity is $= k' C_{\text{ester}} \cdot C_{\text{water}}$, whence

$$k' = 0·0000815.$$

The ratio $\frac{k}{k'}$ is therefore 2·92, and according to p. 178 this should be equal to K, the reaction constant. Knoblauch allowed the reaction to proceed till equilibrium was reached, and from the quantities then present found $K = 2·84$ a satisfactory confirmation of the kinetic theory of reaction.

Similarly Bodenstein found for the decomposition of hydriodic acid

$$2\,HI \rightleftarrows H_2 + I_2$$

at 440°, that the velocity of the partial reaction from left to right (decomposition) is $k = 0·00503$, and for the reverse reaction (formation of HI) $k' = 0·365$, whence

$$\frac{k}{k'} = 0·0138.$$

But measurement of equilibrium gave as the reaction constant $K = 0·0146$ in agreement with the ratio of velocities.

§ 12. Temperature and Velocity of Reaction.

The velocity of a reaction invariably increases, and that very rapidly, as the temperature rises. The mode of dependence on temperature is well illustrated by the known phenomenon of the saturation pressure of an evaporating liquid: evaporation may indeed be looked upon as a simple case of chemical reaction (not, of course, in a homogeneous system), i. e.

$$H_2O \text{ (liquid)} \rightleftarrows H_2O \text{ (vapour)}.$$

Here we have a reversible conversion between two different kinds of molecular arrangements; equilibrium is established when the number of molecules of water evaporating per second is equal to the number of steam molecules condensing. As the temperature is raised the velocity of evaporation increases, and to enable the opposite process to balance it the concentration of the steam must be increased (and therefore its pressure). The rate of rise of the pressure consequently gives a notion of the rate of increase of the evaporation process with rise of temperature, and to a first approximation the pressure is found to follow the logarithmic rule

$$\log p = a + bT,$$

where a and b are constants; or, in words, for each degree rise in temperature the pressure is raised by a constant fraction of its value. E. g. we find for water at

Temp.	*Press.* (mm.).	*Diff. per* 1° (mm.).	% *increase per* 1°.
20°	17·39	1·10	6.15
21°	18·49	1·17	6.10
22°	19·66	1·23	6.06
23°	20·89		

The percentage increase per degree is here nearly constant; more closely examined it is found to fall off a little as the temperature rises. Thus for a higher temperature we have

80°	354·64	14·65	4·05
81°	369·29		

Here, while the actual rise of pressure per degree is more than tenfold that at the lower temperature, the fractional rise is 4 per cent. as against 6 per cent.

Similar relations hold between velocity of reaction and temperature. Thus, for example, the rate of inversion of cane-sugar was found, in one experiment, to vary as follows:—

Temp.	k.	$\log k$.	*Diff. per* 1°.
40°	73·4	1·8657	0·05546
45°	139	2·1430	0·05702
50°	268	2·4281	0·05260
55°	491	2·6911	

It will be noticed that the small rise of 15° in temperature causes the reaction to go seven times as fast, but that the differences in *log k* per degree are approximately constant, i. e. the value of k is increased by the same fraction of itself for each degree. The mean difference in the logarithm is 0·05502, and the number corresponding to this 1·1135; this is the ratio between the velocity constant at $t+1$ and that at $t°$, so that the increase per degree is 11·35 per cent.

Most reactions vary in velocity from 8 to 12 per cent. per degree; the change produced by 100° is therefore extremely large. Thus the decomposition of dibromosuccinic acid in aqueous solution,

$$C_4H_4Br_2O_4 = C_4H_3BrO_4 + HBr,$$

occurs more than 3,000 times as rapidly at 101° as at 15°. It is consequently inevitable that the number of reactions convenient for measurement should be small, for in most cases the velocity at such temperatures as are conveniently attainable is either too rapid to measure, or so slow that it is uncertain whether combination occurs at all. The following table, quoted from van 't Hoff's *Lectures on Theoretical Chemistry*, summarizes all the best known cases:—

Reaction.	*Velocity (time in minutes).*		*Rate of increase %*
$PH_3 = P + H_3$	k_{310} = 0·000006	k_{512} = 0·00031	1·97
$AsH_3 = As + H_3$	k_{256} = 0·00035	k_{367} = 0·0034	2·07
$CH_3CO_2C_2H_5 + NaOH$	$k_{9·4}$ = 2·307	$k_{44·94}$ = 21·648	6·51
$CH_3CONH_2 . Aq$	65° to 100°	—	7·80
$KClO_3 + FeSO_4 + H_2SO_4$	k_{10} = 1	k_{32} = 7·15	9·33
$CH_2ClCO_2Na + NaOH$	k_{70} = 0·000822	k_{130} = 0·217	9·77
$CH_2ClCO_2H . Aq$	k_{80} = 0·0000222	k_{130} = 0·00237	9·81
$C_4H_4Br_2O_4 . Aq$	k_{15} = 0·00000967	k_{101} = 0·0318	10·24
$CH_2OHCH_2Cl + KOH$	$k_{24·5}$ = 0·68	$k_{43·6}$ = 5·23	11·13
$CH_3CHOHCH_2Cl + KOH$	$k_{24·5}$ = 4·9	$k_{43·6}$ = 31	11·02
$(CH_3)_2COHCH_2Cl + KOH$	$k_{24·5}$ = 173	$k_{43·6}$ = 1100	11·02
$(CH_3)_2COHC(CH_3)HCl + KOH$	$k_{24·5}$ = 193	$k_{43·6}$ = 940	10·87
$HPO_3 Aq$	0° to 61°	—	11·61
$NaOC_2H_5 + CH_3I$	k_0 = 0·00336	k_{30} = 2·125	12·81
Diazoamido into amidoazobenzene	k_{25} = 0·0001	k_{55} = 0·0042	13·28
Inversion of sugar	k_{25} = 0·765	k_{55} = 35·5	13·76
$COS + H_2O$	$k_{15·05}$ = 0·00031	$k_{40·14}$ = 0·00815	13·91
Respiration of plants	0° to 25°	—	9·6
Action of enzymes	60° to 75°	—	2·17

The unit of concentration in the above table is the quantity expressed in the formula, in grams, per litre.

Only two gaseous reactions are mentioned in the table, and their coefficients are much smaller than any of the others; this no doubt is largely due to the much higher temperature of the reaction—from 256° to 512° C. Another gaseous reaction has been measured, viz. the decomposition of hydriodic acid $2\mathrm{HI} \rightleftarrows \mathrm{H}_2 + \mathrm{I}_2$.

For this Bodenstein found

$$k_{283} = 0{\cdot}0_6942, \quad k_{393} = 0{\cdot}000588, \quad k_{508} = 0{\cdot}1059.$$

From these numbers the rate of increase is calculated to be 4·37 per cent. at 500° and 6·56 per cent. at 300°, a number comparable with reactions of liquids rather than of gases[1]. It may be noted that the velocity of gaseous reactions is especially difficult to measure, for the reason just mentioned; thus van 't Hoff attempted to determine the rate of combination of oxygen and hydrogen at 440°, but without obtaining any results of value, as the phenomenon observed depends largely on the state of the walls of the vessel, a new glass vessel behaving quite differently to one that had been in use for some time.

§ 13. Explosions.

When a system capable of chemical change is heated, its behaviour will differ according as the change is accompanied by an absorption or evolution of heat: if the former be the case, the natural tendency to cooling by radiation, conduction, &c., will be augmented by the progress of reaction; the temperature will thus be kept down and the velocity of reaction will not exceed that proper to the temperature at which the system is maintained by the heating appliances used. If, on the other hand, the reaction is exothermic, i. e.

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[1] *Ostw.* 29. 314.

accompanied by evolution of heat, we have to distinguish two cases : (1) the evolution of heat is not rapid enough to supply the loss by conduction, &c., then the temperature will not rise indefinitely and the reaction will proceed quietly; (2) the evolution of heat more than compensates for the loss, then the reaction will produce rise of temperature, and the rise of temperature increase the velocity of reaction indefinitely, so that the whole mass suffers conversion in a very short time : this is known as an explosion.

The lowest temperature at which this occurs, which may conveniently be called the temperature of inflammation, varies considerably according to the circumstances of the reaction, since it depends on the rate at which heat can be withdrawn from the gas. The case that has been the most studied is the combination of oxygen and hydrogen ; the limit at which explosion replaces slow combination has been set at various temperatures from 500° to 845° by various observers.

Explosions are not, however, commonly produced by heating the entire explosive mixture to a high temperature. If a small portion of an explosive mixture be heated, say by an electric spark, to a temperature sufficient to effect the explosion, the reaction may be propagated to all parts of the mass. This will be the case if the heat generated by the reaction raises the temperature of the mixture to some point above the temperature of inflammation, for then the reaction—complete, and practically instantaneous—taking place in any small portion will heat a neighbouring portion sufficiently to explode that, and the reaction will be communicated from point to point of the mixture. We have here to do with a process essentially different from any hitherto considered, for the systems so far considered have been uniform in character throughout the volume they occupy. In the present case we have no 'velocity of reaction' in the ordinary sense to consider, for in an explosion the velocity of reaction is immeasurably rapid ; but there is a velocity of propagation of the disturbance to measure, a true ‘velocity’ in the ordinary sense, comparable to the velocity of propagation of a wave, and measurable in centimetres per second. The essential condition of the process is that by some means a high temperature should be propagated through the mass of reacting material. This may happen in two ways: (1) by conduction of heat; (2) by the heating effect of a wave of pressure ; and we accordingly get the two forms of reaction known as ‘progressive combustion’ and ‘explosive wave.’ The former of these occurs in the well-known experiment of filling a tube with oxygen and hydrogen, or oxygen and carbon monoxide, and applying a light to the mixture. The reaction is only slightly explosive, and is propagated with a velocity of a few metres per second ; the process depends on the thermal conductivity of the gas, each layer being heated by direct contact with the exploded layer immediately behind it. The explosive wave, on the other hand, can be set up in the same mixture by a powerful local pressure, such as that due to the explosion of a small charge of mercuric fulminate ; a wave of compression, strictly analogous to a sound wave, is set up in the gas, and the compression of each layer in turn is sufficient to raise it momentarily to a temperature above that necessary for inflammation. Such a wave is propagated with a velocity comparable to that of sound, indeed greater, on account of the high temperature of the gas, and has been found experimentally to vary from 1,000 to nearly 3,000 metres per second. It differs, too, from ordinary progressive combustion in the very high pressure produced, for combination takes place in layers of gas already highly compressed by the wave, and the sudden high temperature may increase the local pressure already existing tenfold: to this is due the shattering effect of the wave.

When explosion, i. e. sudden combustion, takes place in a gas, it is possible to calculate the 'temperature of combustion,' i. e. the temperature to which the gas is carried by the heat liberated in the reaction. Of the two data required for this, the heat of reaction may be measured by ordinary means at low temperatures; the specific heat of the gases, on the other hand, varies so considerably with temperature that measurements made under ordinary conditions are of no value for the calculation. Mallard and Le Chatelier[1], and Berthelot and Vieille[2], have overcome this difficulty by measuring the pressure generated in exploding mixtures of various compositions, and so deducing the temperature which the gas reaches; making an allowance for heat radiated during the process, it is then possible to estimate roughly the specific heat of the gases concerned. Thus Mallard and Le Chatelier find for the molecular specific heat at constant volume of H_2, N_2, O_2, and CO up to 2,000°, the value $5 + 0{\cdot}00062\,t$, where t is the temperature (Cent.); for CO_2 the value is $6{\cdot}3 + 0{\cdot}00564\,t - 0{\cdot}00000108\,t^2$, and for H_2O $5{\cdot}91 + 0{\cdot}00376\,t - 0{\cdot}000000155\,t^2$. With these numbers the temperature of combustion of mixtures considerably diluted with non-combustible gases may be found. Now when the temperature of combustion is so lowered that it no longer exceeds the temperature of inflammation, progressive combustion will, obviously, not occur in the gas: Bunsen, for example, found that an explosive mixture of oxygen and hydrogen, when diluted with 9·35 times its volume of oxygen, would explode, but with 10·47 it would not. Taking the mean of these numbers as the limit, the temperature of combustion, and therefore also of inflammation, may be reckoned as 740°.

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[1] *Comptes rendus*, vols. 91, 93, 95.

[2] l. c. vols. 95, 96.

§ 14. False Equilibrium.

So far we have regarded the velocity of any reaction as increasing in a continuous manner with rise of temperature, the relation between the two quantities being expressible by a formula

$$\log k = a + bT,$$

or a slight modification of this. If that is true, we may draw the important inference that a reaction which takes place at any temperature will also take place at any other, higher or lower, the velocity merely being altered. It is in fact found that numerous reactions which occur rapidly at high temperatures can be produced at lower temperatures. and it is not possible to set a limit at which the reaction begins. Thus a mixture of oxygen and hydrogen, which at a high temperature—say 700° to 800°—explodes, combines quietly, but with easily measurable velocity, at 448°; it takes place, too, to the extent of a few per cent. when the mixture is heated for 65 days to 300°, but could not be detected at 100° on heating for 218 days continuously[1].

The true equilibrium between oxygen, hydrogen, and steam is that existing at very high temperatures, when the reversible reaction

$$2H_2 + O_2 \rightleftarrows 2H_2O$$

takes place freely, and a continual interchange of atoms ensures that the proportions of the different gases are such as are required for complete stability (or such as give the greatest value to the entropy; see chap. iii). In contradistinction to this we have at low temperatures a state of 'apparent' or 'false' equilibrium in a mixture of oxygen and hydrogen; for such a mixture can be preserved unchanged for (apparently) any length of time: yet it is not in truly stable equilibrium (its entropy is not the greatest possible), and a trifling occasion, such as an electric spark, will suffice at any time to convert the mixture; it remains in apparent equilibrium on account of a difficulty in passing from the less to the more stable arrangement of atoms, comparable to friction in ordinary dynamical systems.

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[1] V. Meyer and W. Raum, *Ber.* 28. 2804.

Usually, of the two partial reactions which go to produce equilibrium, one becomes appreciable at a lower temperature than the other. This is most clearly brought out by the researches of Hoitsema[1] on the reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O.$$

At ordinary temperatures there is apparent equilibrium, both in a mixture of carbon dioxide and hydrogen and in a mixture of carbon monoxide and steam; either mixture may be kept for years without change. The reaction from right to left is the first to appear on rise of temperature: if a mixture of CO and H_2O be passed through a tube maintained at about 600°, the issuing gas contains enough CO_2 to render lime-water milky. On the other hand, no action between CO_2 and H_2 could be detected at 900°. Between 600° and 900°, then, k' (velocity of the reaction $\longleftarrow$) has a finite value, while k (velocity of the reaction $\longrightarrow$) is infinitesimal, so that the reaction constant $K = \frac{k}{k'} = 0$, and equilibrium is only reached when the whole system is converted into CO_2 and H_2. At higher temperatures k also comes to have a measurable value: we have then reached the true state of equilibrium expressed by the chemical equation. The actual proportions of the gases in equilibrium will depend on the temperature, and some information on this point may be derived from explosions of substances containing carbon, hydrogen, and oxygen: the result of such an explosion is always to produce H_2 and CO as well as H_2O and CO_2 in varying quantities. By an analysis of the results Hoitsema concludes that $K = 4$ somewhat above 2000°, and increases to a maximum of 6·25 at 2670°. So far, then, the system $CO + H_2O$ has been gaining on the other till the concentration of these gases amounts to $\sqrt{K} = 2{\cdot}5$ times that of the CO_2 and H_2. In other words, at 2670° some 72 per cent. of the mixed gas consists of monoxide and steam. Beyond that temperature, however, the reaction $\longleftarrow$ again increases faster than the reaction $\longrightarrow$, so that K falls off, and the proportion of monoxide and steam becomes smaller.

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[1] *Ostw.* 25. 686.

But although in many cases a reaction is gradually brought into play by rise of temperature, in accordance with the explanations given above, and no discontinuity occurs, it is not always so. E g. the oxidation of phosphorus has been much studied, with the result of showing that there is a sharp limit of temperature bounding the regions of oxidation and of apparent equilibrium. The limit depends on the pressure of the oxygen: thus with oxygen at atmospheric pressure (760 mm.) oxidation occurs above 19·2° with fair rapidity, and is accompanied by phosphorescence; below that temperature it suddenly ceases. If the pressure of the gas be 355 mm. the same phenomenon is observed at 1·4° (Joubert). This case can evidently not be brought under the general rules as to the influence of temperature on velocity of reaction, since they give no suggestion of possible discontinuity. Ewan[1] has followed out this subject quantitatively from a different point of view: a thin layer of phosphorus was spread (by melting) over the inside of a glass globe, in which also a little water was placed. The globe was then evacuated and oxygen allowed to enter; as the phosphorus oxidized, the pressure of the gas fell, so that by observations of a pressure gauge attached to the apparatus the velocity of reaction could be calculated. This was found to be closely proportional to the pressure (and therefore concentration) of the oxygen from 0 to 520 mm. (at 20°); above this pressure, however, the rate of reaction rapidly falls, till at about 700 mm. it ceases altogether, in accordance with Joubert's observations.

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[1] *Ostw.* 16. 321, or *Phil. Mag.* (5) 38. 512.

§ 15. Influence of the Medium on Velocity of Reaction.

The velocity of a reaction is usually influenced very considerably by the solvent in which it is carried out. The solvent in fact usually exercises an influence on the state of equilibrium also; this we shall have to consider in detail in the following chapter: but apart from any effect of that kind, the velocities of the same reaction in different solvents differ to an extraordinary extent. Thus the combination of ethyl iodide with triethylamine at 100° was measured by Menschutkin[1] with some twenty solvents. In hexane the velocity was 0·00018, in benzyl alcohol 0·133, or about 600 times greater. Little systematic information has so far been obtained, except that the velocity appears to be greatest in media which possess the highest dielectric constants; thus water (diel. const. = 75), formic acid (62), methyl alcohol (32·5) appear to be the most energetic solvents: but such a rule is only a very rough approximation to the truth, for e.g. the velocity is greater in benzyl than in methyl alcohol, though the former has a dielectric constant of 10·6 only, and the order of effectiveness of solvents is not the same for all reactions.

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[1] *Ostw.* 6. 41.

CHAPTER V

CHEMICAL DYNAMICS OF HETEROGENEOUS SYSTEMS

§ 1. The Phase Rule.

Following out the definition of homogeneity given at the beginning of the last chapter, we may regard as heterogeneous a system in which parts are distinguishable by their external characters, state of aggregation, density, refractive index, and so on, without regard to chemical composition. If the physical properties change continuously, e. g. in a system formed by salt solution and water diffusing into one another, the system cannot be in equilibrium : such cases we shall not have to consider. But if the change be discontinuous, e. g. from solid salt to solution, from solution to the vapour above it, equilibrium may exist. In this case each part of the heterogeneous system is called a *phase*.

Gases can form only one phase, since they are all indefinitely miscible one with another. Liquids may form one or more, according as they mix completely or not. Solids in general do not form homogeneous mixtures, so that each solid occurring in the chemical system will constitute a separate phase ; exceptions to this rule occur in the case known as *solid solution*, i. e. when two isomorphous crystalline solids are capable of crystallizing together in variable proportions, so that one may be looked upon as dissolved in the other.

To characterize a heterogeneous system we require to know also the number of its chemical components ; this word is, however, to be taken in a somewhat special sense. A component may be either an element or a compound, but if the latter it must not suffer decomposition in passing into any of the phases of the system; further, the number of components is to be the least possible, and though there may be several ways of choosing the components of a given system, the number of them will be definite. We are led, as is admirably shown by Ostwald (*Lehrbuch* 2, ii. 477), to conclude that the number of components may be determined by chemical analysis, independently of any theories as to the constitution of the substances concerned. It is only necessary to analyze the various phases, and find what is the least number of component substances by means of which the observed analytical compositions can be made up. E. g. in a system containing ice, water, and steam, elementary analysis shows the same composition in each of the three phases: it is not necessary to inquire into the molecular weight of the water, &c.; there is clearly only one component. Again, NO_2 and N_2O_4 form a system which, according to temperature and pressure, will contain more of the one or the other substance, but there is only one component in the sense of the present chapter, for elementary analysis always yields the same result, 14 of N to 32 of O. A system containing magnesium sulphate solution, together with vapour of water and any of the solid hydrates of the sulphate, has two components; for the composition of each of the phases can be stated by the quantity of $Mg\,SO_4$ and of H_2O present, it is not necessary to push the analysis further. A system containing the chlorides and nitrates of potassium and sodium in aqueous solution has four components, viz. H_2O and three of the salts; for the total amount of K, Na, Cl, and NO_3 present may be regarded as made up into any three of the four salts. E. g. suppose there is more K than Cl present, then all the Cl may be regarded as forming KCl, and the remaining substances will be KNO_3 and $NaNO_3$; the composition of the solution can then be exactly stated by the quantities of those three salts, without reference to the compound NaCl. This, it must be noted, implies nothing as to the actual arrangement of the elements to form molecules: nothing, indeed, beyond the required information as to the analytical composition of the various phases.

The number of phases and components is related to the number of *degrees of freedom* of the system. A homogeneous substance, or phase, is capable of varying (1) in pressure; (2) in temperature; (3) in composition. Each of the former affords one degree of freedom, the latter one or more; if there is but one component there can of course be no change in composition, if there are two components one degree of freedom arises in the variable ratio of the second component to the first, if three components then each of the other two may vary in its proportion to the first, and there are two degrees of freedom, and so on; the freedom of the system is to be reckoned by the number of independent variations it can suffer without the disappearance of any of its phases. Now this relation, first stated by Gibbs[1], holds between the number of phases P, components n, and degrees of freedom F—

$$F = n + 2 - P.$$

This is known as the *phase rule*. Expressed in words, it states that the number of degrees of freedom of a chemical system is equal to the number of components, increased by two, and diminished by the number of phases. In illustration of the meaning, consider first a system with one component only, then the number of degrees of freedom is $3 - P$. If all the substance is in one phase it possesses two degrees of freedom, i. e. is capable of two independent variations (within certain limits); since in this case no change of composition is possible, the variations must be in temperature and pressure. Accordingly a single substance such as water, if it occurs exclusively in one phase—solid, liquid, or gaseous—may suffer *independently* changes of pressure and temperature

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[1] *Trans. Connecticut Acad.* 3. 108 (1874).

(within certain limits, beyond which conversion into another phase takes place). A mixture of NO_2 and N_2O_4 similarly, when all in a single phase (gas), possesses two degrees of freedom, for though the percentage of NO_2 present varies, it only does so as a function of the pressure and temperature; an independent change in the percentage unaccompanied by change of pressure and temperature is not possible. If two phases occur, say water and steam, there remains only one degree of freedom. This is shown by the well-known phenomenon of saturation pressure; to each temperature there corresponds one pressure only at which water and steam are in equilibrium, and if the pressure be increased the phase steam disappears, if it be decreased the phase water disappears. Hence, if a variation be made in the temperature of a mixture of water and steam, the pressure must vary in a defined manner in order to retain both phases; the pressure variation is not an independent one, and there is only one degree of freedom. In order to obtain the three phases, ice, water, and steam, in equilibrium together, a definite condition of pressure and temperature must hold, so that the system is capable of no variation. We shall have to return later to this condition—the *triple* point. More than three phases cannot exist in a system with one component; of water, it is true, only three phases are known, but some substances possess more, e. g. sulphur, which is known as vapour, liquid, rhombic crystals, and monosymmetric crystals: these four forms can under no circumstances exist in equilibrium together.

Next consider a system with two components, say NaCl and H_2O, for which consequently the degrees of freedom number $4-P$. In one phase both components are known to exist, viz. that of solution. If then salt solution occurs by itself it is capable of three independent variations, in pressure, temperature, and concentration; if a second phase appears the variability is restricted in some direction. Thus in presence of solid NaCl the concentration of the solution must be that corresponding to saturation (under the prevailing conditions of pressure and temperature); or if vapour and solution are present together the pressure can only be the saturation pressure (for a solution of the given concentration and temperature). If three phases occur, say salt, solution, and vapour, there still remains one degree of freedom, for the temperature may be changed, and yet the system be in equilibrium, provided the corresponding changes in pressure and concentration are allowed to take place; otherwise one phase will disappear, i. e. either all the vapour will be condensed, or all the salt dissolved, or all the solution broken up into salt and vapour. To get four phases in equilibrium, ice, salt, solution, and vapour, certain conditions of temperature pressure and concentration must be satisfied, and the system is not capable of variation. If the system consists of more than two components, similar relations may be found between the number of phases and the degrees of freedom.

Such systems may be conveniently called *invariant*, *univariant*, *divariant*, &c., according as they possess no, one, two, &c., degrees of freedom.

It must be understood that changes in the quantity of each phase present do not come under the head of the 'variations' to which the phase rule refers, for such changes in no case affect the equilibrium. E. g. ice and water may exist in equilibrium under certain conditions of temperature and pressure, whether the amount of ice be large or small compared with that of water; we need therefore pay no attention at all to the total mass of any phase so long as it does not vanish altogether.

§ 2. Transition Point.

From the preceding illustrations it will be apparent that a system containing two phases may be looked upon as the limiting state between two systems, each containing one of the phases only. The *transition* from one to the other takes place there, under definite conditions of temperature and pressure: on the one side of these conditions, the phase A is more stable than B; on the other side B is more stable than A; only under the given conditions do the two phases possess the same degree of stability, so that neither of them tends to conversion into the other. Hence the *transition state* between two phases may be defined as that in which *the relative stability of the phases is reversed.* Similar relations hold between systems containing a larger number of phases; one with three phases is the limit between two systems with two phases each. Thus the conditions of temperature and pressure under which the phases A, B, and C coexist constitute the transition between the systems AB and AC, under which therefore the relative stability of B and C in presence of A is reversed. But also it may be looked upon as the limit between the systems AC and BC or between AB and BC; hence it is necessarily the state in which the transition states between A and B, A and C, B and C become identical.

These relations may most conveniently be expressed by diagrams. A system with one component only possesses at most two degrees of freedom, and so may be represented completely by a plane diagram, the two co-ordinates of which are usually chosen to represent pressure and temperature. Such a diagram has already been given partly for the three phases, solid, liquid, and vapour, between which the well-known physical transitions take place (Fig. 5, p. 40). That diagram may be completed by drawing the line DE, which represents the boundary between solid and liquid as shown in Fig. 24; DE slopes very slightly to the right upwards in the case of benzene, since by raising the pressure to five atmospheres the melting point is raised about 0·143°. The reversal of stability is shown in Fig. 5 by the crossing of the lines AB and CD; the dotted curve AD shows the condition of equilibrium between undercooled liquid and vapour. The liquid here is less stable than the solid, for, possessing a higher vapour pressure than the solid, if both were placed in contact with their vapour the liquid would distil over and condense as solid. To the right of D the solid would possess a higher vapour pressure than the liquid, and so would become the unstable phase; actually it is so unstable as to be unobtainable.

Confining our attention to the stable phases we see that Fig. 24 consists of three areas, EDC representing solid benzene only, EDB liquid only, BDC vapour only; three lines, DE representing equilibrium between solid and liquid, DB liquid and vapour, DC vapour and solid; and one point, D representing equilibrium between all three phases. The latter is called the *transition point* of the system, and in this (or any system of one component) is a triple point.

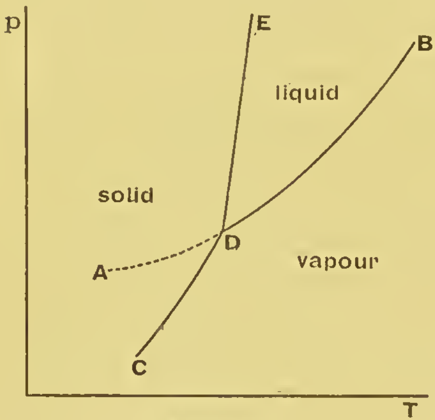

FIG. 24.

A practical distinction of considerable importance may be drawn between systems that contain a gaseous phase and those that do not: the latter are called *condensed* systems. The reason for the distinction lies in the small influence of pressure on solids and liquids: their compressibility is usually many thousand times less than that of gases at atmospheric pressure; e.g. the elasticity of water is about 20,000 atmospheres, while that of air is one atmosphere

(p. 8). Accordingly the changes of concentration produced in condensed systems by variations of pressure within ordinary limits may usually be ignored. One consequence of this is that the transition state under atmospheric pressure may practically be regarded as a transition point, and is often so spoken of. Thus in the example already given the transition from solid to liquid benzene occurs under atmospheric pressure at 5·61°, while the true transition point (triple point) is at 5·58° and 36·06 mm. pressure. Methods of observation will be described below for finding the transition point of condensed systems, and mostly with this modified meaning.

The problems involved in the study of heterogeneous equilibrium are thus practically two: (1) in condensed systems, to determine the various transition temperatures, and so mark out the diagram of the system into regions showing the stability of the various phases; (2) in uncondensed systems, in addition to finding the transition temperatures of the solid and liquid phases, to determine the transition states for the uncondensed phases (gas and dilute solution) together with the conditions which hold within each of those phases. With regard to the later point, it is found that Guldberg and Waage's law may be applied to each phase of variable composition, as if it constituted a homogeneous system in itself; with, however, a certain assumption as to the behaviour of the condensed phases in equilibrium with it.

§ 3. Delimitation of a System with one Component, Sulphur.

The relations between the various phases of sulphur have been very completely worked out by Reicher[1] and others, and are shown graphically in Fig. 25. There are four phases to consider—vapour, liquid, and two solid crystalline forms, the rhombic and monosymmetric. In addition to these, one or more forms of amorphous solid sulphur are obtained by rapid cooling, but they do not appear to be stable under any circumstances at low temperatures, so that they need not be taken into account. In the diagram (which is not drawn to scale) ABC represents the vapour pressure curve of rhombic sulphur, CEF that of the liquid; the two cut in C ($114{\cdot}5^{c}$), which accordingly is the melting point of the rhombic form under its own vapour pressure (a small fraction of the atmosphere only), and therefore a triple point. BDE is the vapour pressure curve of monosymmetric sulphur, which melts at 120°, the point of intersection with CEF being E, another triple point. But, it will be noted, BDE crosses ABC at B, so that a transition point exists there, the rhombic form being the more stable at temperatures below B, the monosymmetric above: this is also a triple point if the transition take place under the pressure of the sulphur vapour only. All three transitions, B, C, E, however, are most conveniently determined at atmospheric pressure, and as the systems are 'condensed' the error made in doing so is extremely small. Thus B was found by Reicher by the dilatometric method (vid. inf.) as 95·6°, and it rises by about $\frac{1}{20}$ degree per atmosphere. There is, however, a characteristic difference between the transition at B and the fusions at C and E; in fusion, although the liquid phase

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[1] Van 't Hoff, *Studien über Chemische Dynamik*, 1896, p. 185.

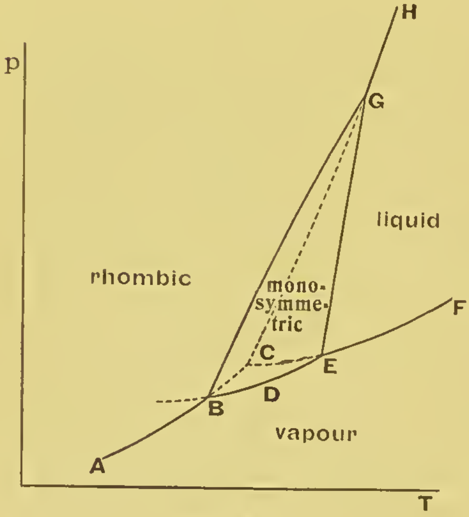

Fig. 25.

can be obtained below the melting point, the solid cannot be obtained above that point. The reason doubtless lies in the difficulty of arrangement in formation of a crystal, which makes the transition a slow one, while the conversion into liquid, requiring no new arrangement of the molecules, can take place as rapidly as heat can be supplied to bring it about. Transition between two solid phases is much more opposed by frictional resistance, so that it is easily possible to preserve rhombic sulphur above 95·6° and monosymmetric below that temperature for a considerable time. Were this not the case the point C could not be determined, for both phases there are unstable, the point lying entirely within the region of monosymmetric sulphur; the rhombic and liquid forms can be kept in equilibrium there long enough to determine the melting point, but eventually both would be converted into monosymmetric crystals. The triple points B, C, E, represent three of the four possible combinations of the four phases taken three at a time; there remains one, viz. rhombic, monosymmetric, and liquid. This point G corresponds to the pressure at which the melting point of the monosymmetric form, shown by the line EG, coincides with the transition point of the rhombic form shown by BG. Such a point exists because the transition point is raised by pressure more rapidly than the melting point, and has been estimated to lie at 131° and 400 atmospheres[1]; at higher pressures rhombic sulphur melts directly, it and the liquid phase being in stable equilibrium as shown by the line GH. The regions of the diagram are therefore :—

Four areas	ABGH	rhombic crystals.
	BGE	monosymmetric crystals.
	HGEF	liquid.
	FEBA	vapour.
Six lines	AB	rhombic crystals and vapour.
	BG	,, and monosymmetric crystals.
	GH	,, crystals and liquid.

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[1] Bakhuis Roozeboom, *Ostw.* 2. 475.

	BE	monosymmetric crystals and vapour.
	EG	,, ,, and liquid.
	EF	liquid and vapour.
Three points	B	rhombic and monosymmetric crystals and vapour.
	G	,, ,, ,, liquid.
	E	monosymmetric crystals, liquid, and vapour.

All the above are in stable equilibrium. In addition there are the unstable systems (represented by dotted lines), of which BC, GC, EC, are merely prolongations of AB, HG, FE, respectively, but the point C is new and corresponds to

C rhombic crystals, liquid, and vapour.

§ 4. Delimitation of a System with two Components.

A system with two components has, as we have seen, three possible degrees of freedom—temperature, pressure, and concentration ; so that for its graphical representation it needs, strictly, a figure in space of three dimensions. The 'singular' conditions under which two or more phases occur would then be shown by the figure in question : the conditions for the existence of two phases by surfaces, for three phases by lines arising by the intersection of two of the surfaces, and finally the transition points in which four phases are in equilibrium by the points of the figure where three surfaces intersect. Since, however, it is impracticable to work with solid models, we are reduced to making use of diagrams which are sections or traces of the model ; thus we may have diagrams in which (p, T) or (p, C) or (T, C) are chosen as axes, and any two of these will between them suffice to exhibit the relations of the various phases. The first and last of these form perhaps the most useful pair to choose. The concentration may be expressed in various ways (see p. 26), but most conveniently by the number of grams of one component in 100 grams of mixture (or else by the number of mols. in 100 mols. of mixture, i. e. the molecular percentage). The figures below will serve as examples of this mode of representation.

We may divide the cases to be considered, for practical purposes, into two groups: (1) when one component is practically non-volatile as compared to the other; (2) when the volatilities of the two are comparable in magnitude. The reason for the distinction will be clear from the following considerations: since solids do not in general mix at all, there will be phases of variable composition only in the fluid state, viz. one gaseous phase and usually one, sometimes more, liquid. If, however, one of the components has no appreciable volatility, the gaseous phase will consist of the other component only, and the phases of variable composition will be liquid only, and usually one in number if any: this makes both the experimental treatment and the graphical representation considerably easier. We shall illustrate both cases by means of a definite example, treated in some detail. The systems that have been studied include in the first group the dissociation of calcium carbonate, of compounds of ammonia with salts[1], e.g. $AgCl . 3 NH_3$ and $2 AgCl . 3 NH_3$ or $ZnCl_2 . 6 NH_3$, $ZnCl_2 . 4 NH_3$, $Zn Cl_2 2 NH_3$ and the formation and solution of hydrated salts; in the second group the dissociation of NH_5S, NH_4CN, PH_4Br, $NH_4CO_2NH_2$[2] (in these cases no liquid phase arises, so that here again there is only one phase of variable composition); further, the equilibrium between CO_2 and H_2O, SO_2 and H_2O, NH_3 and H_2O, and others in which each component is obtained in both liquid and gaseous state.

§ 5. Salt Hydrates.

The formation and dissociation of hydrated salts constitute the most important group of cases in which only one of the components is volatile, and a large mass of data exists, with regard to the solubility, and vapour pressure, and the transition points between various hydrates of the same salt. As a typical instance we may consider sodium sulphate, which in the form of Glauber's salt has long been known to show certain remarkable phenomena in solution. Sodium sulphate is known to exist in three crystalline forms, as anhydrous Na_2SO_4, and as the hydrates $Na_2SO_4 . 7\,H_2O$ and $Na_2SO_4 . 10\,H_2O$ (Glauber's salt): we have therefore in all six phases to deal with, viz. in addition to those three, ice, solution, and vapour; of these, however, one, $Na_2SO_4 . 7\,H_2O$, appears to be throughout unstable, being slowly converted into a mixture of decahydrate and anhydride.

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[1] Isambert, *C. R.* 66. 1259 (1868).

[2] Ibid. 92. 919; 94. 958; 96. 340, 643; 97. 1212.

At ordinary temperatures the decahydrate separates from solution when the latter is saturated; it is true that the solution very easily becomes supersaturated, but in the presence of a crystal of the salt the exact condition of saturation may easily be obtained. The concentration of the saturated solution increases with rise of temperature till above 30°. If, however, the anhydride be mixed with water it is possible to obtain a solution containing more Na_2SO_4 than is in equilibrium with the decahydrate; this may therefore be regarded as another saturated solution, and it may be kept indefinitely so long as no crystal of decahydrate comes into contact with it; it is, however, essentially unstable, since the concentration of the salt is more than enough to cause the hydrate to crystallize out, if only the opportunity for it be given. The concentration of this solution saturated with regard to the anhydride decreases with rise of temperature, so that eventually it becomes less than that of the other saturated solution. Loewel's[1] experiments give the following values (gms. Na_2SO_4 in 100 gms. of solution):—

Temp.	*Saturated for decahydrate.*	*Saturated for anhydride.*
31·84°	28·57	33·50
32·73°	33·67	33·20

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[1] *Ann. Chim. Phys.* (3) 49. 50.

From these numbers it follows that 32·65° is the temperature at which the solubilities of the two salts are equal, and at which consequently both can exist in equilibrium with the solution (under one atmosphere pressure); it is the temperature at which the relative stability of the anhydride and hydrate is reversed, in other words the transition point, in the modified sense applicable to condensed systems, for the reaction

$$Na_2SO_4 . 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O.$$

At the transition point not only the solubilities, but as in the former examples, the vapour pressure, must be the same for the two systems, i. e. the vapour pressure of the hydrated salt must become equal to that of the saturated solution of anhydride. This has been tested directly by a differential pressure gauge with the following results:—

Temp.	29°	30·83°	31·79°	32·09°	32·35°	32·5°	32·6°	33·05
Press. diff.	23·8	10·8	5·6	3·6	1·6	?	0	0

The difference of pressure is expressed in mm. of oil, and is taken between the slightly effloresced salt (system Na_2SO_4 . $10H_2O$ and Na_2SO_4) and the slightly moistened salt (system $Na_2SO_4 . 10H_2O$ and solution). Below the transition point the solution has the greater pressure; above 32·6° it was not found possible to preserve the hydrate from decomposition (cf. the existence of undercooled water but not of superheated ice); but the point of equality of pressure is found to agree with that of equal solubility.

These relations are shown in Fig. 26; the two parts of the diagram may be regarded as projections of the surface which represents the relations between temperature, pressure, and composition for sodium sulphate. The lower part shows the concentration (per cent. by weight) as a function of the temperature. $A_1B_1C_1$ is the saturation curve for the decahydrate, $D_1B_1E_1$ that for the anhydrous salt; B_1, the intersection, is therefore the transition point (under atmospheric pressure). The upper part of the figure shows the corresponding vapour pressures, also as a function of the temperature. $A_2B_2C_2$ is the curve for saturated solution of the decahydrate, $D_2B_2E_2$ for saturated solution of the anhydrous salt, while FB_2 represents the vapour pressure of the crystalline decahydrate itself. It must be noted that while the

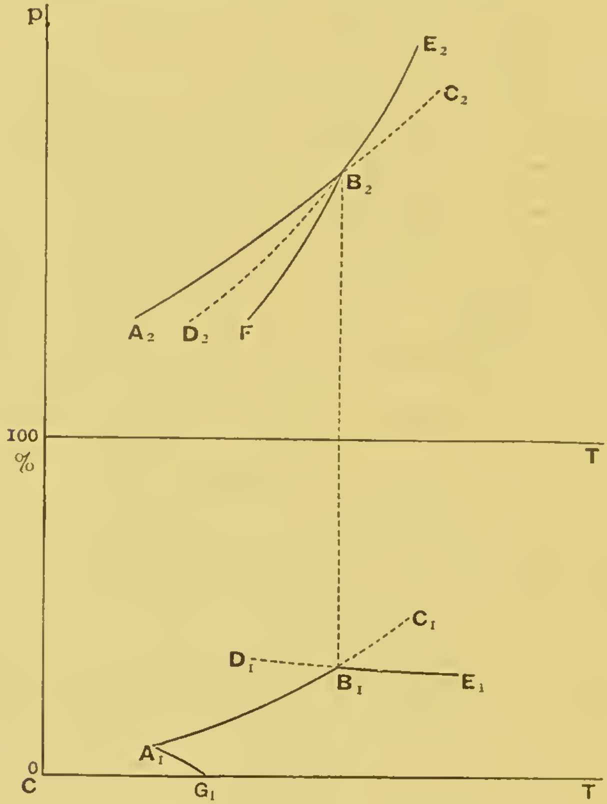

FIG. 26.

form with the *smaller concentration* of Na_2SO_4 in the liquid phase is the more stable, the saturated solution of that form possesses the *greater vapour pressure*; hence while the concentration curve for the stable states, $A_1B_1E_1$, shows a sharp bend downwards at the transition point, the curve showing the vapour pressure of the saturated solution for the stable states, $A_2B_2E_2$, shows a sharp bend upwards there. This result is general, as it depends on the necessary conditions of stability.

The heptahydrate shows similar relations to the anhydride, but as the vapour pressure of its solution is always less (and its solubility greater) than that of the decahydrate, it is throughout unstable, and liable to decompose into decahydrate and anhydride; its transition point is 24·2°.

The exact definition of the transition point for the decahydrate is the point at which the four phases, decahydrate, anhydride, solution, and vapour, are in equilibrium; the point is therefore perfectly definite in pressure and temperature. Moreover the variation of the transition temperature with pressure is extremely small: for this reason it has been suggested by Richards[1] as a new 'fixed point' in thermometry, and he gives as a preliminary result 32·379° (on the hydrogen scale) as the transition temperature under atmospheric pressure. The vapour pressure is 30·82 mm.; the true transition point (quadruple point) will accordingly lie slightly below 32·379° if $Na_2SO_4 . 10\,H_2O$ expands on melting, above it if it contracts.

The system possesses another quadruple point, viz. that at which ice and decahydrate are in equilibrium with solution and vapour. When a salt solution is cooled it either (1) reaches saturation and then deposits crystals of salt, or (2) freezes, with deposition of pure ice. The latter case really means that the mixture of salt and water has become saturated with respect to the latter substance; and the one or the other case of saturation will occur according to the composition of the original solution. In the first event, the fractional amount of water in the mixture will increase as the temperature falls, in the second event that amount will decrease; so that both cases tend towards a limiting composition at which ice and salt crystallize out together. This is shown on the diagram by the lines B_1A_1, separation of salt from the saturated solution, and G_1A_1, separation of ice; A_1 is the point at which the whole solution freezes together, and is accordingly the lowest temperature at which the liquid phase can exist (under atmospheric pressure); it is called the *cryohydric point.* There is really a cryohydric line, since pressure produces a certain change in the temperature of transition, but like other effects of pressure on condensed systems it is very slight. The quadruple point is the cryohydric point under the saturation pressure of the system.

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[1] *Ostw.* 26. 690.

The meaning of a cryohydrate may be further illustrated by a case in which the two components do not differ much in melting point: thus, for mixtures of naphthalene and paratoluidine the following results have been obtained:—

% Naphthalene	100	80	50	34	31	29	25	20	0
Melting point	79·3°	68·2°	50·3°	38·1°	29·1°	34·6°	35·3°	36·6°	38·9°

It will be observed that addition of either substance to the other lowers its freezing point, and that the lowest temperature (cryohydric point) is 29·1°, obtained by a mixture of 31 parts naphthalene to 69 paratoluidine.

Many salts possess more than one hydrate which is stable over a certain range of temperature and pressure. Copper sulphate is an instance of this that has been well worked out. Besides the anhydrous salt, crystalline hydrates containing one, three, and five molecules of water are known. Each of these phases as well as the solution has a distinct vapour-pressure curve. If a crystal of $CuSO_4 . 5H_2O$ be taken and gradually deprived of water, at first the system will consist of the pentahydrate together with $CuSO_4 . 3H_2O$. Of these two the pentahydrate has the higher vapour pressure (the vapour pressure normally increases with increasing water content), so that as long as any of the pentahydrate remains the vapour pressure is that of the pentahydrate. When the water present falls below three molecules to one of $CuSO_4$, the pressure suddenly drops to that of the trihydrate, remaining constant again till the stage $Cu\,SO_4 \,.\, H_2O$ is reached. With complete disappearance of the trihydrate the pressure again drops, and becomes constant for the system $Cu\,SO_4 \,.\, H_2O + Cu\,SO_4$. This was shown by Pareau[1] by placing $Cu\,SO_4 \,.\, 5\,H_2O$ under an air-pump and gradually reducing the pressure; he found (at 50°):—

Composition	$Cu\,SO_4 \,.\, 4\frac{1}{2}H_2O$	$3\frac{1}{2}H_2O$	$2\frac{1}{2}H_2O$	$1\frac{1}{2}H_2O$	$\frac{1}{2}H_2O$
Pressure	46·3	47·1	29·9	29·7	4·4 mm.

The last number, saturation pressure of the monohydrate, is about $\frac{1}{20}$ that of water at the same temperature, and serves as a measure of the drying power of the anhydrous salt; i.e. anhydrous copper sulphate will withdraw water from an atmosphere in which the pressure of the vapour is more than $\frac{1}{20}$ that due to water itself, until it is completely converted into $Cu\,SO_4 \,.\, H_2O$; after that it loses its efficacy and will only absorb water when the air contains more than enough to saturate the trihydrate, or about $\frac{1}{3}$ the saturation pressure of pure water.

The same principles are very well brought out by an experiment of Andreae[2] on strontium chloride, which forms two hydrates with six and two molecules of water respectively. These hydrates, slightly dessicated, were placed in two flasks connected with one another, but closed against the outside air. The salts were found, before the experiment, to have the composition $Sr\,Cl_2\, 5{\cdot}8\, H_2O$ and $Sr\,Cl_2\, 1{\cdot}65\, H_2O$ respectively, so that the former was a mixture of hexhydrate and dihydrate, the latter of dihydrate and anhydride. Under these circumstances the anhydride withdraws water from the hexhydrate till it is all converted into $Sr\,Cl_2\, 2\, H_2O$, when equilibrium is reached, for it could only absorb more water by itself becoming converted into the hexhydrate. Accordingly, in 19 days the second flask was found to have absorbed 0·038 gm. of water from the first, and its contents to have reached the composition

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[1] *Wied.* 1. 39 (1877).

[2] *Ostw.* 7. 241.

$SrCl_2 . 2{\cdot}01 H_2O$. In 200 days more, no further change occurred.

The first instance studied of equilibrium of a binary system in which only one component is volatile was the dissociation of $CaCO_3$ on heating. Since CaO is not volatile, there is a definite curve of saturation pressure of carbon dioxide answering to the equation $CaCO_3 \rightleftarrows CaO + CO_2$. This has been determined by Le Chatelier[1] as follows:—

Temp.	547°	610°	625°	740°	745°	810°	812°	865°
Press.	27	46	56	255	289	678	763	1333 mm.

§ 6. Observation of Transition Points in Condensed Systems.

Since the transition point is the limit of stability between two systems, it follows that (1) the properties of the two systems must become identical at that point; (2) on passing the transition point, one of the systems must (if sufficient time be allowed) completely replace the other. On these facts are based various methods of observing the transition temperature, the chief of which may be summarized as follows:—

(1) By identity of properties.

(*a*) The vapour pressures become identical (see examples above).

(*b*) The solubilities become identical (see examples above).

(*c*) The electromotive force between the solutions and a metal become identical (see chap. vii).

(2) By transition.

(*d*) Heat is always absorbed in passing from the system stable at low temperature to that stable at high temperature. Hence observations by a thermometric method.

(*e*) The system usually expands or contracts on transition; hence the dilatometric method.

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[1] *Compt. rend.* 102. 1243.

(*f*) The transition can sometimes be detected by change of crystalline form.

(*a*) Small differences of vapour pressure may conveniently be measured by a gauge such as is shown in the accompanying figure (Fig. 27). In the bulbs *d* and *e* are placed the salts or solutions to be compared, or if the absolute vapour pressure be desired, strong sulphuric acid may be placed in one of the bulbs. The gauge is half filled with a non-volatile oil, and is then laid sideways, so that the oil may flow into the bulbs *a*, *b*, and the whole evacuated and sealed up. It is again placed vertically, and the millimetre scale *c* attached to it: the whole may then be immersed in a water bath, and raised to any desired temperature.

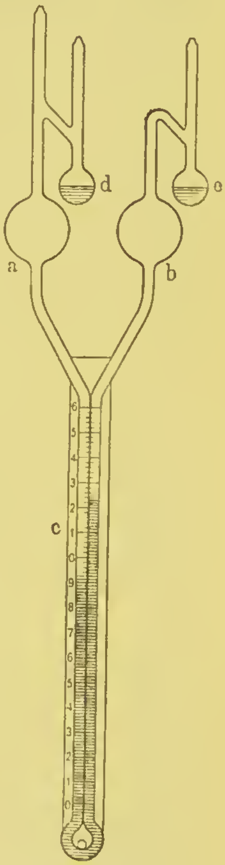

Fig. 27.

(*b*) Measurements of solubility may be made in two ways: (1) by saturating the solution at a constant temperature, filtering and analyzing the solution; (2) by weighing out quantities of solvent and dissolved body, and raising the temperature of the mixture gradually till complete solution occurs.

(*c*) See chap. vii.

(*d*) When a system is gradually heated or cooled past a transition point, its temperature will remain for some time constant, and give an accurate measure of the transition temperature. This fact is familiarly known and used in the transition ice $\rightleftarrows$ water, in which the temperature remains constantly 0° so long as both phases are still present. The same is true of any similar change, e. g. in the case of sodium sulphate mentioned above. The constant temperature is the more easily maintained, the more considerable is the latent heat of transition, for if the latent heat be very small, local overheating or undercooling is apt to occur. The experiment may conveniently be made in a Beckmann freezing-point apparatus (p. 45), and the following points must be attended to; (1) the materials must be pure; (2) the mixture suffering transition must be half fluid, so that it can be well stirred to prevent local differences of temperature; (3) the bath should not be much above or below the transition temperature. The method of rising temperature usually gives the best results, as it avoids the possibility of undercooling, which so easily occurs in salt solutions, so the 'bath' may advantageously be a thermostat kept about half a degree above the temperature of transition.

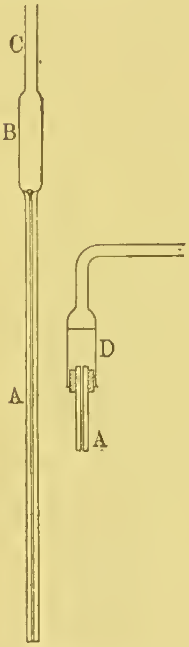

Fig. 28.

(*e*) The thermometric method is inapplicable to a transition between two solid forms on account of the extreme slowness of the change. The dilatometric method has been successfully applied by Reicher to the transition between rhombic and monosymmetric sulphur, and may be used whenever there is an appreciable change of volume accompanying the conversion. The dilatometer consists of a bulb B (Fig. 28) about 12 × 1 cm., ending in a short tube C through which it is filled, and the capillary A. After the substance (e. g. sulphur) has been introduced, C is sealed, the apparatus evacuated, and a liquid (paraffin) introduced, which serves as indicator in the capillary; the liquid may be one having a slight solvent action on the body to be studied, in order to hasten the conversion, if it be very slow, as in the case of sulphur; the filling is accomplished by the tube AD connected to an air-pump, and containing some paraffin. The dilatometer is then sealed up and placed in a thermostat, in order to observe whether expansion or contraction takes place. Thus in one of Reicher's experiments on sulphur, at a temperature 95·1° the paraffin indicator expanded through a length of about 10 mm. in an hour, at 96·1° it contracted 19 mm. in the same time, while at 95·6° no change could be detected: the transition point is therefore 95·6°.

(*f*) Lehmann observed that when fused ammonium nitrate is allowed to solidify it forms isotropic crystals of the regular system, but at 120° these become doubly refracting. On further cooling to 87° needle-shaped rhombic crystals appear, similar to those obtained from hot alcoholic solution; these, again, change into a fourth modification on taking out into the air. If the fourth modification be heated it passes, at 36°, 87°, and 120°, through the same changes in the reverse order. Many similar cases have been noticed.

§ 7. Simple and Mutual Solubility.

Before dealing with the general case of a system with two components, in which more than one phase of variable composition may occur, it is necessary to consider the phenomena of mixtures in the liquid state.

Many, perhaps most, pairs of liquids mix in all proportions, so that the mixture never constitutes more than one phase. This case is in many respects comparable with the mixture of gases, but whilst for gases the properties of the mixture never vary much from the mean between those of the pure substances, in liquids the departure may be considerable. Certain physical properties, such as specific volume, refractivity, have already been considered (chap. ii), and we have seen that it is possible to calculate their values for a mixture from those of the components approximately. The approximation is a good one when the liquids are without chemical influence on one another (e.g. benzene and toluene), but is much less good when something comparable to chemical combination takes place (e. g. sulphuric acid and water). Similar variations in the vapour pressure of the mixture are observed: if two liquids *A*, *B* have vapour pressures such as are represented by the heights of A, B in Fig. 29, the pressure of a mixture may lie between the two, and nearly on the straight line between A and B (carbon tetrachloride and benzene, curve I), or it may show a maximum for a certain percentage composition (propyl alcohol and water[1], curve II), or a minimum (formic acid and water, curve III).

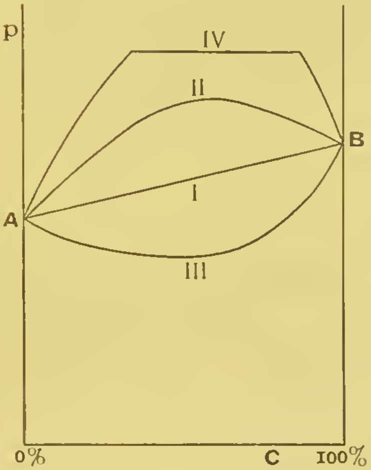

FIG. 29.

Again, many liquids mix in certain limited proportions only: thus water dissolves, at ordinary temperatures, 3 or 4 per cent. of aniline, and aniline about as much of water. If the two substances be mixed in more equal proportions they will separate into two liquid layers, one consisting of water saturated with aniline, the other of aniline saturated with water. On rise of temperature the solubility of each substance in the other will usually increase till a point is reached, the *critical point of mixture*, at which the two layers come to have the same composition, and the whole mixture becomes homogeneous. This only happens for aniline and water under pressure, since the critical temperature is above 100°; in other cases the complete mixture is more easily brought about by heat. E. g. phenol and water form a homogeneous mixture in all proportions at 68° or any higher temperature; below that point the mixture separates into two layers. Mixtures forming two layers usually possess a vapour pressure greater than that of either component, but less than the sum of the two. This is shown by line IV in the figure, of which the curved parts represent the pressure of homogeneous mixtures of varying composition, while the horizontal line indicates that when both layers are present the vapour pressure has a fixed value corresponding to the fixed composition of each layer, and the same for both.

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[1] *Wied.* 14. 34, 219.

If the solubility of each substance in the other be reduced we approach the limiting case of complete immiscibility, which is practically realized by such pairs of liquids as water and benzene. The vapour pressure of any such mixture is sensibly equal to the sum of the pressures of the components.

When a liquid mixture is cooled sufficiently, one of the components crystallizes out; we have then the following cases to consider:—

If the liquids are miscible in all proportions, as with naphthalene and paratoluidine (p. 220), the mutual solubility becomes merely restricted in range: firstly (from 79·3° to 38·9°), to mixtures containing less than a certain percentage of naphthalene; secondly (from 38·9° to 29·1°), to mixtures in which the percentage of each component is restricted within certain limits. During the part of the range 79·3° to 38·9° the mixtures may be regarded as solutions of naphthalene (proportion limited by the phenomenon of saturation) in paratoluidine (which may be added in indefinite quantity without solidifying); we thus get the case of one-sided or *simple solubility*, in which the solvent and dissolved body play distinguishable parts. Ordinary salt solutions belong to this group; the temperature of the solution lying below the melting point of one component (the salt), but above that of the other (ice). Usually the melting point of the salt lies above the boiling point of water, but that makes no essential difference, for the boiling point is arbitrary and can be raised or lowered by alteration of pressure. Thus the melting point of $AgNO_3$ is 198°; its range of simple solubility therefore extends from 0° to that temperature (at which water remains liquid if the pressure be about

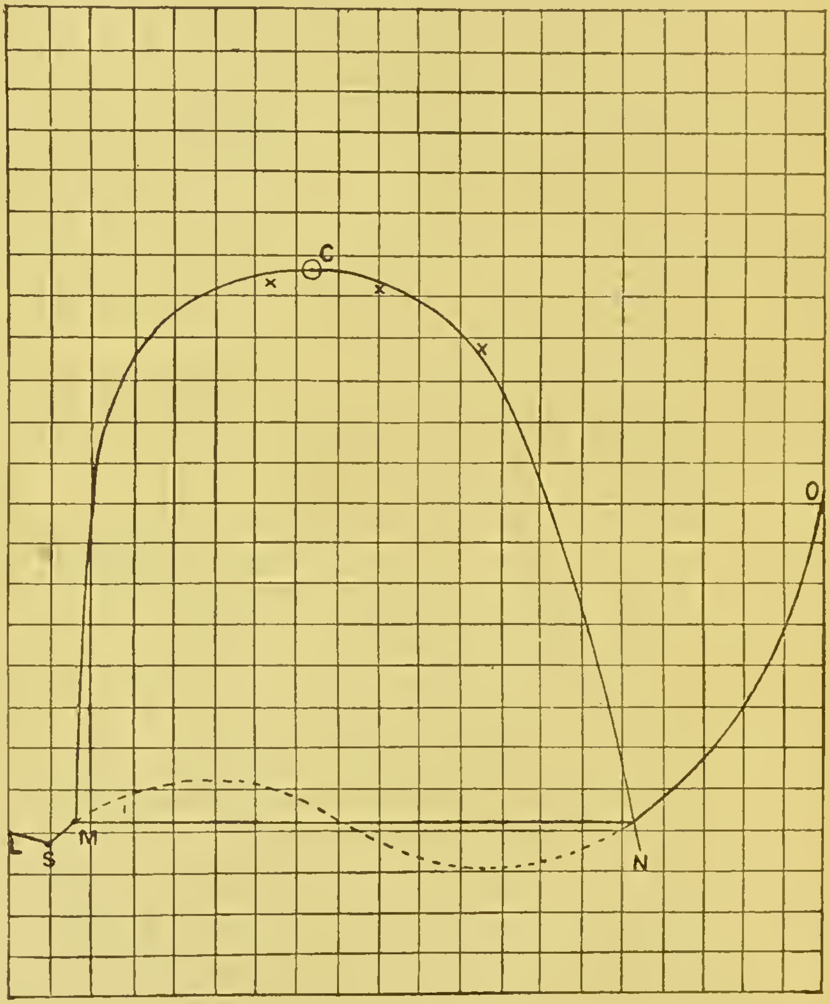

Fig. 30.

15 atmos.). Above 198° water and silver nitrate are liquids miscible in all proportions.

If the liquids are incompletely miscible the case is more complex: it may be studied with the aid of Fig. 30, which shows the behaviour of phenol and water[1]. The curve MCN bounds the area of incomplete mixture, C being the critical point, above which complete miscibility occurs. On cooling from this temperature (68°) two phases appear, solution of phenol in water and solution of water in phenol, till at 40° separation of phenol begins (point O); below that point two mixtures still exist, one (shown to the left of CM) containing any proportion of phenol from zero to that required to saturate (about 10 per cent. at 40°), the other limited in both senses, to the left by CN, formation of the other liquid phase, and to the right by ON, separation of solid phenol; consequently no simple solution of water in phenol can well be spoken of in this range of temperature. On cooling further to + 1·5° the second liquid phase disappears by solidification, and we are left with only the solution of phenol in water (to the left of MS), from which at 0° ice begins to separate; below 0° miscibility exists only for proportions limited in both senses, till at S we reach the cryohydric point (– 1·0°), at which the composition of the liquid reaches a definite value (4·83 per cent. phenol), and then the mixture solidifies as a whole.

§ 8. General Case of System of two Components.

The general case, in which there is more than one phase of variable composition, was first made clear by the remarkable researches of Roozeboom[2] on gaseous hydrates, from which we may take as typical the behaviour of mixtures of SO_2 and H_2O. Five phases are known, viz. gaseous mixture, two liquid phases (one of which may be regarded as a solution of SO_2 in water, the other as a solution of water in liquefied SO_2), the solid hydrate $SO_2 \cdot 7H_2O$, and ice. Only four phases can exist in equilibrium together, and two points are known in each of which four phases do exist (quadruple points).

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[1] Lehfeldt, *Phil. Mag.* (5) 47. 294.

[2] Roozeboom, *Ostw.* 2. 449.

The relations are shown in Fig. 31, in which B and L are the quadruple points. We may consider first the system in the neighbourhood of L; at that point, at temperature 12·1° and pressure 1770 mm. of mercury, the phases vapour (V), solution of SO_2 in water (L_1), of water in liquid SO_2 (L_2), and solid hydrate (S) coexist. If heat be supplied to the system, while the pressure is kept constant, reaction will take place in the sense

$$S + V = L_1 + L_2,$$

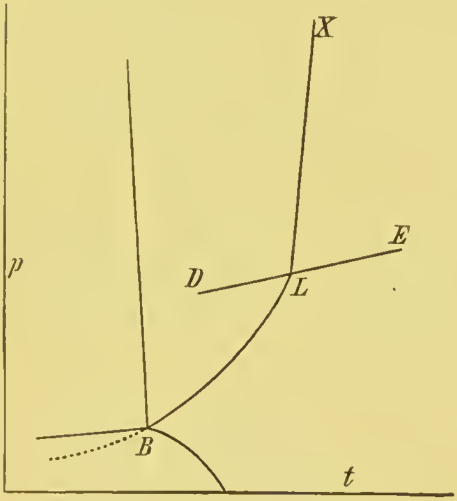

Fig. 31.

i. e. the hydrate will liquefy, and as the liquefaction is accompanied by expansion some of the vapour will disappear; this process will go on until either the solid or gaseous phase disappears, and it will depend on the quantity of the components which disappears first. If the former, the system will proceed along the line LE, which represents equilibrium between V, L_1, and L_2; if, however, it is the vapour that disappears, LX will represent the subsequent behaviour of the system, which then consists of L_1, L_2, and S. LE is analogous to an ordinary vapour-pressure curve, and, sloping slightly upwards to the right, represents the increase with temperature of the vapour pressure of the liquid when two layers are present. LX is analogous to the curve showing the relation between pressure and the melting point of a solid; it is, in fact, the melting-point curve for the hydrate, which breaks up into two liquid layers, and, like a melting-point curve, rises nearly vertically, as pressure has little influence on a condensed system. Similarly, if heat be withdrawn from the system at L the above-mentioned reaction will take place in the reverse sense till either L_1 or L_2 disappears (according to the quantities present), and we get the curve LD (for V, L_2, S) or LB (for V, L_1, S). Thus on passing the quadruple point any one of the four phases may disappear, but on the other hand, each of them (according to the quantities present) is capable of existing both above and below that temperature ; the point is, however, a transition point for the pairs S, V, which can only exist below 12·1°, and L_1, L_2, which can only exist above 12·1°. In other cases a quadruple point may be the point at which *one* phase necessarily breaks up into *three* others, so that it is the transition point for that single phase.

The four curves ending in L divide the field into six areas (which partially overlap) corresponding to the six possible groups of two phases. It will be seen from the diagram that under some conditions of temperature and pressure (area ELB) the system must consist of a certain pair of phases ; in another part (areas XLE and DLB) it will resolve itself, for the same temperature and pressure, into two phases in either of two ways, according to the quantities of the components, while in another part (area XLD) it will resolve itself in any one of three ways.

Summarizing the results expressed by the diagram, we have :—

Six areas showing the conditions of temperature and pressure under which can exist each pair of phases, viz. :—

within BLE, vapour and solution of SO_2 in H_2O ;
above DLE, vapour and solution of H_2O in SO_2 ;
within DLB, vapour and solid hydrate ;
within XLE, the two solutions ;
to the left of XLB, solution of SO_2 in H_2O and solid hydrate ;

within XLD, solution of H_2O in SO_2 and solid hydrate.

Four lines showing the conditions for simultaneous existence of three phases, viz. :—

LE, vapour and the two solutions;
LX, the two solutions and solid hydrates;
LD, vapour, solution of H_2O in SO_2, and solid hydrate;
LB, vapour, solution of SO_2 in H_2O, and solid hydrate.

One point showing the conditions for simultaneous existence of four phases, viz. :—

L, vapour, the two solutions, and solid hydrate.

Following the curve LB we come to another quadruple point B (— 2·6° and 211 mm.) at which the phases vapour, solution of sulphur dioxide in water, solid hydrate, and ice are in equilibrium, and the field round it may be divided into lines and areas in a very similar way.

§ 9. **Law of Mass Action in Heterogeneous Systems.**

It has already been mentioned that the law of mass action is applicable to the fluid phases of a heterogeneous system, but with a certain modification, or rather extension. In each of the 'dilute' phases, i.e. gas or solution, equilibrium holds between the constituents in the manner expressed by Guldberg and Waage's law; each phase may in fact be regarded for the purpose as a homogeneous system, but the concentration of certain constituents is regulated by the presence of the same substances in liquid or solid form. If a volatile solid or liquid is present it possesses a concentration (or effective mass) in the gaseous phase which corresponds to its vapour pressure, and if a soluble solid (or gas) is present it possesses a concentration in the liquid phase which is limited in the same manner by its solubility.

Not only is this the case, however, for substances with an appreciable volatility or solubility, but it appears that all substances may be treated as if they possessed some volatility and solubility, however small. So that when a reaction between solids and a gas (or a liquid) is in question, it is really the equilibrium between the vapour (or solution) of the solid (though perhaps in immeasurably small quantity) and the gas (or liquid) that has to be considered. It results from this that in the equation for the law of mass action the factors representing any substance present in the solid state must be given a value which depends only on the temperature (not on the total amount present), viz. the concentration of the saturated vapour (or solution) of the substance in question. This mode of treatment has received experimental justification in many cases, and will become intelligible by considering some examples.

The reaction $NH_4SH \rightleftarrows NH_3 + H_2S$
is reversible, and takes place on sublimation of the solid ammonium sulphydrate. If we regard the solid as volatilizing unchanged and then dissociating in the gaseous state, we are led to the equation for the gaseous phase,

$$\frac{C_{NH_3} \cdot C_{H_2S}}{C_{NH_4SH}} = \text{const.},$$

but since the sulphydrate vapour is in presence of solid it must possess a constant concentration, so that we may transfer it to the other side of the equation and write

$$C_{NH_3} \cdot C_{H_2S} = \text{const.}$$

If no free ammonia or sulphuretted hydrogen is present to start with, the concentrations of the two gases are necessarily equal, and the concentration of each (and so its pressure) is fixed for any given temperature. Hence, although two gases are formed, the dissociation will produce a definite saturation pressure like a simple volatilization. Thus Isambert[1] found the pressure to be 13·2 cm. at 4·2°, 77·2 cm. at 32·6°. If free ammonia or sulphuretted hydrogen be present in excess, the product of the partial pressures must be constantly equal to one quarter of the square of the total pressure in the former case. For instance, at 17·3° the dissociation pressure was 30·0 cm.; that of each constituent consequently 15·0, and the product $p_{NH_3} \cdot p_{H_2S} = 225$. But when sulphuretted hydrogen sufficient to produce 11·1 cm. pressure in the apparatus was added, the partial pressure of the H_2S rose to 21·4, while that of ammonia fell to 10·3; the product $10 \cdot 3 \times 21 \cdot 4 = 220$, which may be regarded as identical with the preceding 225; and similarly in many other experiments.

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[1] *Comptes rendus*, 92. 919.

The dissociation of ammonium carbamate

$$NH_4CO_2NH_2 \rightleftarrows 2\,NH_3 + CO_2$$

leads to the equation

$$C^2_{NH_3} \cdot C_{CO_2} = \text{const.},$$

since the carbamate itself is present in the gaseous phase with constant (and very small) concentration. If p be the dissociation pressure, the substance yields, when there is no excess of either gas, the partial pressure of $CO_2 = \frac{p}{3}$, while that of NH_3 is $\frac{2p}{3}$, so that the constant in the equation (concentration being again represented by pressure) is $\frac{4}{27}p^3$. Experiments by Horstmann[1] and Isambert[2] fully confirm this conclusion.

Again, the reaction

$$3\,Fe + 4\,H_2O \rightleftarrows Fe_3O_4 + 4\,H_2$$

(occurring in a system of three components) will yield the equation

$$C^4_{H_2} \div C^4_{H_2O} = \text{const.},$$

if we put the concentrations of the Fe and Fe_3O_4 in the gaseous phase constant, or in other words, if we ignore the presence of the solids. On taking the fourth root of the equation we get $C_{H_2} \div C_{H_2O} =$ constant, i. e. the reaction will proceed in one sense or the other till a certain proportion holds between the concentration of the hydrogen and the steam. This was the conclusion arrived at by Deville[1]: he maintained the system at 440°, but to secure a definite pressure of water vapour kept the apparatus in communication with a retort containing water at 0° in one experiment, at 11·5° in another. The pressure of H_2O was therefore the saturation pressure at these temperatures, viz. 4·6 and 10·1 mm. respectively, while that of the hydrogen was found manometrically to be 25·8 and 57·9 in the two experiments; but $C_{H_2} \div C_{H_2O}$ in the first case is $25{\cdot}8 \div 4{\cdot}6 = 5{\cdot}6$, in the second is $57{\cdot}9 \div 10{\cdot}1 = 5{\cdot}7$—a very close agreement, considering the experimental difficulties to be overcome.

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[1] Liebig's *Annalen*, 187. 48 (1877).

[2] *Comptes rendus*, 93. 731.

When a solid plays a part in a reaction taking place in solution we must, consistently with the above theory, attribute to it a definite concentration in the solution which depends only on the temperature (and to a minute extent on the pressure), and it is well known that even so-called insoluble salts, such as silver chloride or barium sulphate, do dissolve in water to an appreciable extent. But it should especially be noticed that the equilibrium that holds between the solid and solution refers only to the presence in solution of material of the same composition as the solid. If dissociation occurs, in particular electrolytic dissociation, the solution must be regarded, so long as solid salt is present, as saturated by the undissociated salt it contains, without regard to the amount of dissociated substance (ions) present, an amount which may be influenced by other bodies in the solution. We must therefore distinguish between the *apparent solubility* measured by the total amount of salt taken up by unit volume of the solution, and the *real* solubility measured by the amount of salt which exists unchanged in unit volume of solution: the latter is independent of the presence of other bodies.

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[1] Liebig's *Ann.* 157. 71 (1871).

It follows that when two salts with a common ion are mixed, the apparent solubility of each will be affected, since their degree of dissociation is affected (p. 165). This has been followed out experimentally with sufficient exactness to serve as a confirmation of the theory of electrolytic dissociation, and has indeed been used as a means of measuring the degree of dissociation. The extent of mutual influence can be calculated, in the case of weak electrolytes, by means of Ostwald's law of dissociation, especially when the solubility is small. E. g. the solubility[1] (gram-molecule per c.c.) of α-bromisocinnamic acid in presence of oxanilic acid is shown in the following table:—

Conc. of oxanilic acid.	*Solubility of α-bromisocinnamic acid.* *obs.*	*calc.*
0	$17{\cdot}6 \times 10^{-6}$	—
$27{\cdot}2 \times 10^{-6}$	$14{\cdot}0$	$13{\cdot}6 \times 10^{-6}$
$52{\cdot}4$	$12{\cdot}9$	$12{\cdot}0$

The dissociation constants are $14{\cdot}4 \times 10^{-6}$ (α-bromisocinnamic) and $11{\cdot}8 \times 10^{-6}$ (oxanilic acid). Hence to calculate the degree of dissociation γ of the former acid we have

$$\frac{(17{\cdot}6 \times 10^{-6}\gamma)^2}{17{\cdot}6 \times 10^{-6}(1-\gamma)} = 14{\cdot}4 \times 10^{-6},$$

whence $\gamma = 0{\cdot}584$. The undissociated salt accordingly has the concentration $17{\cdot}6 \times 10^{-6}(1-0{\cdot}584) = 7{\cdot}32 \times 10^{-6}$; this is the true solubility of the acid. If then C be the total concentration of the α-bromisocinnamic acid, and C' that of the oxanilic, while C'' of the latter is dissociated, the solution will contain

$7{\cdot}32 \times 10^{-6}$	undissociated α-bromisocinnamic acid,
$C - 7{\cdot}32 \times 10^{-6}$	α-bromisocinnamic ions,
$C' - C''$	undissociated oxanilic acid,
C''	oxanilic ions,
$C + C'' - 7{\cdot}32 \times 10^{-6}$	hydrogen ions.

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[1] Noyes, *Ostw.* 6. 245.

The law of mass action then gives the equations

$$(C - 7{\cdot}32 \times 10^{-6})\,(C + C'' - 7{\cdot}32 \times 10^{-6}) = 14{\cdot}4 \times 10^{-6} \times 7{\cdot}32 \times 10^{-6},$$

$$C''\,(C + C'' - 7{\cdot}32 \times 10^{-6}) = 11{\cdot}8 \times 10^{-6} \times (C' - C'').$$

Since the amount of C' of oxanilic acid added is known, these equations serve to calculate the unknowns; the values of C thus found are given in the above table.

§ 10. Henry's Law. Law of Partition.

It was found long ago by Henry that the solubility of gases in liquids is regulated by the condition that at any given temperature the concentration of the gas in solution is proportional to its concentration in the gaseous state. The measurements of solubility made by Bunsen and others have usually been expressed by an 'absorption coefficient,' which means the volume of gas (reduced to 0° and 760 mm.) absorbed by one volume of solvent under 760 mm. pressure. If, however, the solvent is at t degrees, it is more convenient to multiply the absorption coefficient by $(1 + 0{\cdot}00366\ t)$ in order to express the volume of the gas at $t°$; the number so obtained is the constant required to express Henry's law in modern terminology, i. e. the concentration (gram-molecules per c.c.) of gas in solution which is in equilibrium with the concentration unity in the gaseous phase, a constant that may be called the *coefficient of solubility.* Here, however, as with solids, it is necessary to distinguish between the apparent and real solubility, for the gas may undergo a change on dissolving. This is particularly noticeable when the gas forms an acid or base, which suffers electrolytic dissociation simply, as in the examples

$$HCl = H^{\cdot} + Cl', \qquad H_2S = H^{\cdot} + HS';$$

or with previous hydration as

$$SO_2 + H_2O = H_2SO_3, \qquad H_2SO_3 = H^{\cdot} + HSO_3',$$

$$NH_4 + H_2O = NH_4OH, \qquad NH_4OH = NH^{\cdot}_4 + OH'.$$

In either case the total or apparent solubility is not strictly proportional to the pressure, but when the electrolytes formed are weak, much the greater part of the gas absorbed remains undissociated unless the solution is very dilute. Consequently for pressures over a certain range Henry's law, as applied to the total solubility, appears to be true ; for high pressures some departure from it is noticeable, since the solutions can no longer be regarded as dilute ; for very low pressures the apparent solubility becomes greater, since while the true solubility remains the same, the amount absorbed and dissociated bears a larger and larger ratio to that existing unchanged in solution as the solution becomes more dilute. The experiments of Sims[1] on SO_2 and NH_3 bear out this theoretical conclusion ; for the former gas at 20° the observed coefficient of solubility remains practically constant from 1,900 mm. pressure down to about 300 mm., below which it begins to increase rapidly ; for ammonia at 20° the coefficient increases slowly and nearly linearly from 2,000 mm. pressure down to about 500 mm., and then rises more and more rapidly.

It should be remarked that Henry's law (as applied to the real solubility) is in harmony with the views on dilute solutions deduced from thermodynamic reasoning, and that it is therefore strictly and universally true, so far as the gas solution formed may be regarded as sufficiently dilute[2].

From Henry's law may be deduced a rule as to the partition or distribution of a dissolved substance between two solvents ; for if we admit that all substances are volatile, though possibly only to a minute extent, it follows that the concentration in any solution must be such as to produce equilibrium with the gaseous phase ; but we may suppose the solutions of the same substance in two different solvents to be placed side by side in contact with the vapour rising from them; then the two solutions can only be in equilibrium with one another if each is in equilibrium with the vapour; but since the concentration of the dissolved body in each liquid phase is proportional to that in the gaseous phase, the concentrations in the liquid phases must be proportional to one another. This is essentially the *law of partition* arrived at independently by Aulich[1] and by Nernst[2]: it may be stated as follows:—

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[1] Liebig's *Ann.* 118. 345 (1861).

[2] Van 't Hoff, *Ostw.* 1. 488 ; Rayleigh, *Nature*, 55. 253 ; Donnan, l. c. 57. 53.

'At a given temperature and for a given substance a ratio holds between the concentrations in the gaseous and the various liquid phases of a system which is independent of the total amount of the substance in question, and of the presence of other substances whether chemically related to it or not.'

One or two remarks are necessary, however, to avoid misunderstanding this statement. In the first place it must (like Henry's law, of which it is merely a completion) be taken to apply only to dilute phases, i. e. it is strictly true only when the concentration is indefinitely small, the divergence from it increasing as that condition is departed from. When the substance in question is a solid at the temperature considered, increase of concentration eventually leads to the well-known phenomenon of saturation, followed by deposition of the solid; and it is clear that when that happens for the vapour the solution must be saturated too, since equilibrium with the solid is the condition of saturation. When a third fluid phase separates out (e.g. ether from aqueous solution when the concentration reaches a certain point) the same phenomenon occurs, but in the case of solutions of completely miscible substances (e.g. alcohol in water) no such limit exists, and the vapour and solution gradually reach concentrations to which the law of partition does not apply. On the other hand, the validity of the law is not limited by mere mechanical pressure, since that can be obtained by means of a neutral gas without altering the equilibrium between the vapour and solution. Further, in the statement of the law, ‘substance’ must be taken to mean a definite kind of molecule only, not including the products of polymerization or dissociation ; this is equivalent to the limitation previously expressed by the term ‘real solubility.’ Nernst gives experimental results that illustrate this point: succinic acid dissolved in a mixture of ether and water was found to have these concentrations (per cent.):—

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[1] *Ostw.* 8. 105.

[2] l. c. 8. 110.

Aqueous solution C_A	0·24	0·70	1·21
Ethereal solution C_B	0·046	0·13	0·22
Ratio $C_A \div C_B$	5·2	5·2	5·4

In this case the condition of the acid is the same in the two solutions (apart from a very small fraction electrolytically dissociated in water). But benzoic acid dissolved in benzene and in water does not show the same molecular weight as determined by the freezing-point method, the aqueous solution being normal, but that in benzene consisting mainly of double molecules ; accordingly the (total or apparent) concentrations in the two liquids are not in a constant ratio, as shown by the following numbers:—

Aqueous solution C_A	0·150	0·195	0·289
Benzene solution C_B	2·42	4·12	9·70
Ratio $C_A \div C_B$	0·062	0·048	0·030
Ratio $C_A \div \sqrt{C_B}$	0·0305	0·0304	0·0293

In the more concentrated benzene solutions, the number of associated molecules bears a larger ratio to the number of unassociated, and as it is the latter which is proportional to the number in aqueous solution, the total amount of benzoic acid in benzene solution must bear a larger ratio to that in aqueous when the concentration is large than when it is small. We may draw a quantitative conclusion on this point if we assume that the amount of unassociated benzoic acid in benzene is quite small compared with the whole amount. Calling the former quantity C, and reserving the symbol C_b for the latter, we have that

(1) $C \propto C_A$ (law of partition);

(2) $C^2 \propto (C_B - C)$ (law of mass action), but as C is small this is practically $C^2 \propto C_B$.

Accordingly C_A should be very nearly proportional to $\sqrt{C_B}$, a conclusion borne out by the preceding table.

§ 11. Relation between Reaction Constants and Coefficients of Solubility.

The example just mentioned, on the solubility of benzoic acid in benzene and water, may serve as an instance of the connexion that exists between the equilibrium conditions for a reaction (in that case an association) taking place in two solvents and the coefficients of solubility of the reagents. Stated more generally, we see that there is (1) an equation between the concentrations in any one phase, the form of which is given by the law of mass action, and the constant of which may be determined by experiment; (2) an equation —obtained by measurements of solubility—for each substance, showing the relation between its concentration in the given phase and another. Hence the condition of equilibrium in the second phase, as expressed by the reaction constant, can be calculated without further experiment.

Taking the equation to Guldberg and Waage's law in the logarithmic form (p. 145), and using suffixes to distinguish the concentrations in two phases, say gaseous and liquid, we have

$$\Sigma(\nu \log C_l) = \log K_l, \qquad \Sigma(\nu \log C_g) = \log K_g;$$

but $C_l = \lambda C_g$ for each substance, where λ is the coefficient of solubility of that substance; hence

$$\Sigma(\nu \log C_g + \nu \log \lambda) = \log K_l),$$

and by subtraction

$$\Sigma(\nu \log \lambda) = \log\left(\frac{K_l}{K_g}\right),$$

an equation that may be regarded as determining K_g if K_l is known, or vice versa.

Further, the equations to the reaction may be given in a very simple form by a change in the unit of concentration, provided that the concentration of the saturated solution or vapour does not exceed the limit of what may be regarded as a dilute phase. If solution and vapour are in contact, and one of them be saturated with a certain constituent, the other phase must be saturated with it too; hence the coefficient of solubility may be regarded as the ratio between the saturation concentration in the liquid to that in the vapour. Calling these concentrations S_l, S_g respectively,

$$\frac{S_l}{S_g} = \lambda = \frac{C_l}{C_g}.$$

We see then that in any case the concentration in the liquid phase bears to the saturation concentration in that phase the same ratio as the corresponding quantities do in the gaseous phase. If the saturation concentration be taken as the unit in each phase, we may put

$$\frac{C_l}{S_l} = \frac{C_g}{S_g} = \mathbf{C},$$

where $\mathbf{C}$ may conveniently be called the *reduced concentration*, a quantity that is the same for all the phases. Now since

$$\Sigma(\nu \log C_l) = \log K_l \text{ and } \Sigma(\nu \log C_g) = \log K_g,$$

it follows that

$$\Sigma(\nu \log \mathbf{C}) = \log K_l - \Sigma(\nu \log S_l) = \log K_g - \Sigma(\nu \log S_g) = \mathbf{K},$$

the reduced reaction constant.

Accordingly the equation

$$\Sigma(\nu \log \mathbf{C}) = \mathbf{K}$$

expresses the condition of equilibrium equally in the gaseous state and in any solvent. This may be put into words as follows:—

'If the concentration of each reagent in each phase be expressed as a fraction of its saturation concentration in that phase, the reaction constant is the same for all (dilute) phases.'

CHAPTER VI

APPLICATION OF THERMODYNAMICS TO CHEMICAL EQUILIBRIUM

§ 1. Heat of Reaction.

We saw in chap. iii the exceptional place, amongst physical properties, occupied by the quantities of heat involved in the passage of a substance from one physical state to another, or in the transformation of a chemical system. We have now to consider in detail those quantities of heat, and their relation to the physical or chemical equilibrium concerned.

The name 'heat of reaction' may conveniently be used in the most general sense to mean the heat evolved in any change, physical or chemical, by that amount of the reagents (in grams) which is expressed by the equation. The heat of reaction may then be written at the end of the right-hand member of the equation. It may be a positive or negative quantity according to circumstances; e. g. we may write

$$H_2O \text{ (solid)} = H_2O \text{ (liquid)} - 1{,}440$$

to state that the conversion of 1 gram-molecule of water from the solid to the liquid form is accompanied by *absorption* of 1,440 calories.

The evolution or absorption of heat in a reaction is the sum of two quantities: (1) the change of internal energy of the reacting system; (2) the heat required to perform external work if the system expands, or produced at the expense of external work if the system contracts. The second of these quantities is negligibly small in condensed systems, but may be considerable when the reaction involves gases. It is usually more convenient to deal (theoretically) with the change in internal energy only, and as that is clearly the amount of heat involved if the reaction take place without either expansion or contraction, it may be described as the *heat of reaction at constant volume.* Experimentally it is usually the heat of reaction under constant pressure that is measured; from it the other can easily be calculated, and in what follows the heat of reaction will always be taken to mean that at constant volume (change of internal energy), unless the contrary is stated.

Since one mol. of any gas under pressure p, and absolute temperature T, occupies the volume $\frac{RT}{p}$, the amount of work done when it is generated is measured by that volume multiplied by p, i.e. by RT; while the disappearance of a mol. of gas implies that an amount RT of work is done on the system, and the corresponding amount of heat generated in it. R has the constant value 1·9845 calories nearly; RT at 19° C. (average atmospheric temperature) $= 580$ calories.

As an example, we may take the volatilization of water under one atmosphere pressure: this is accompanied by an absorption of $18 \times 536 = 9{,}648$ calories (per mol.); but as a mol. of gas is evolved in the change, and the temperature of volatilization is 373°, the external work done is $1{\cdot}98 \times 373 = 739$ calories. Hence of the total heat absorption, only the difference $9{,}648 - 739 = 8{,}909$ goes to increase the internal energy of the water, and we may write

$$H_2O \text{ (liquid)} = H_2O \text{ (vapour)} - 8{,}909.$$

This quantity is sometimes called the *internal latent heat* of evaporation.

It is obvious that any heat of reaction will vary according to the state of aggregation of the reagents before and after: it is therefore necessary to specify the state of each when there is any ambiguity. As an instance of a purely chemical change we may take the formation of water from its elements. When hydrogen is burnt and the water formed condensed at atmospheric temperature, 34,180 calories are evolved per gram of hydrogen: we may therefore write

$$2H_2\,(\text{gas}) + O_2\,(\text{gas}) = 2H_2O\,(\text{liquid}) + 136{,}720 - 3 \times 580$$
$$= 2H_2O\,(\text{liquid})\ 134{,}980\ ;$$

for since three mols. of gas disappear in the reaction, 3 × 580 calories of the observed production of heat are due to external work done by the atmosphere in compressing the system, and only the remainder is due to the loss of internal energy of the reagents.

Since the internal energy of a body is always the same when it is under the same conditions (physical state, temperature, and pressure), the change in internal energy corresponding to any reaction is independent of the method by which the reaction is carried out. Hence if the reaction is impossible to carry out directly, or if it takes place too slowly for calorimetric observation, we may take the reagents through any set of changes that lead from the initial to the final state, and add together the changes ($+^{ve}$ or $-^{ve}$) in the internal energy of the system accompanying each. The total will be identical with the change of internal energy that would result from performing the reaction directly. The commonest use of this principle is in determining *heats of formation.* Thus, suppose it is required to know the heat of formation of benzene, i.e. the thermal value of the reaction

$$6C\,(\text{solid}) + 3H_2\,(\text{gas}) = C_6H_6,$$

the product being in the form of vapour at 18°. It is impossible to synthesize benzene directly from its elements; but it may be burnt to CO_2 and H_2O, and the heat of combustion compared with that of the elements. Now the heat of combustion at constant pressure of solid carbon (per 12 gms.) is 96,960 calories, and no change of volume occurs, so that the heat of combustion at constant volume, or change of internal energy, is the same; that of hydrogen is, we have seen, 134,980 for $2\,H_2O$. Hence

$$6\,C\,(\text{solid}) + 3\,H_2\,(\text{gas}) + 7\tfrac{1}{2}O_2\,(\text{gas}) = 6\,CO_2\,(\text{gas}) + 3\,H_2O\,(\text{gas}) + 786{,}840.$$

On the other hand, a mol. of benzene vapour burnt under atmospheric pressure gives out 799,350 calories, but the number of molecules of gas is decreased from $8\frac{1}{2}$ to 6 in the combustion (the water being condensed), hence the change of internal energy is $799{,}350 - 2\frac{1}{2} \times 580 = 797{,}900$. Accordingly the benzene contains $797{,}900 - 786{,}840 = 11{,}060$ calories more internal energy than its constituent elements; or otherwise expressed, its heat of formation is $-11{,}060$. An abbreviated mode of expression for this is

$$[C_6,\ H_6] = -11{,}060,$$

the comma being used to separate the components (elementary or not) out of which the formation takes place. Such a reaction is called *endothermic*: one in which the heat of reaction is positive, *exothermic*.

Heat of reaction is not in general the same at different temperatures, for the internal energy of the substances on each side of the equation is increased on rise of temperature. and unless the rate of rise is the same on both sides, the difference of energy between the two sides will increase or decrease. If q be the heat of reaction at $t°$, s the thermal capacity of the substances on the left hand of the equation, and s' that of the substance on the right hand (all at constant volume), then at temperature $t+1$ the heat of reaction becomes

$$q + s - s'.$$

E. g. the thermal capacity of 32 grams of oxygen and 4 of hydrogen is 15·58 cal., while that of 36 grams of liquid water is 36 cal. Hence the heat of combustion of oxygen and hydrogen falls off by 20·42 cal. per degree. Even this is less than $\frac{1}{6000}$ of the actual heat of reaction, and in many cases the temperature variation is much less, so that q may usually be treated as constant. It would be strictly so if the thermal capacities of the two systems were the same, and therefore if the specific heat were a strictly additive property; for as the two systems on opposite sides of the equation consist of the same atoms, they would in that case possess the same total capacity for heat.

The specific heats of gases are nearly additive, hence we are able to conclude that the heats of reaction between gases are nearly constant, and to make a useful simplification in the expression for the reaction constant between gases (p. 144), the term $\Sigma \nu K_V$ (subsumed under $\Sigma j\nu$) becoming zero. To what degree of approximation this is true may be judged from the following table, calculated from Regnault and Wiedemann's experiments on the gases under constant pressure: the numbers refer to the temperature 0°.

Gas.	*Molec sp. ht. at constant volume* (K_V).
O_2	5·02
N_2	4·88
H_2	4·91
CO	4·86
CO_2	6·45
N_2O	6·74
NH_3	6·57

The values of K_V for the last three gases, calculated on the additive hypothesis, are $CO_2 = 4·86 + \frac{1}{2} \times 5·02 = 7·37$ instead of 6·45, $N_2O = 4·88 + \frac{1}{2} \times 5·02 = 7·39$ instead of 6·74, $NH_3 = \frac{1}{2} \times 4·88 + \frac{3}{2} \times 4·91 = 9·80$ instead of 6·57. Such divergences are sufficient to produce a marked effect when very large ranges of temperature are considered, as is seen from Hoitsema's observations on the reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$

(p. 201) - the reaction constant increases up to 2670° and then decreases. This implies that the heat of reaction is negative below that temperature, but positive above it (p. 151); but over small ranges of temperature the additive law may be regarded as correct.

The additive rule is also approximately true for solid compounds of elements that obey Dulong and Petit's law. The atomic heat of most solid elements being about 6·4, the molecular heat of compounds of those elements containing n atoms should be $6{\cdot}4 \times n$; and accordingly a number of diatomic oxides, sulphides, chlorides, and iodides, have molecular heats lying between 11 and 14·5, triatomic compounds of the types Ag_2S, Cu_2O, $CaCl_2$ have molecular heats between 15·9 and 19·0, and so on with more complex compounds.

§ 2. Thermochemical Methods.

The calorimetric methods employed to study heat of reaction are two, principally: the method of mixture, and that of Bunsen's calorimeter.

The *method of mixture* is a modification of the process usually adopted for finding specific heats, viz. that of immersing a hot body in a mass of cold water and observing the rise of temperature that ensues. In the corresponding chemical problem it is necessary to carry out a reaction within a mass of water, and observe the rise of temperature when all the heat generated in the reaction has become diffused throughout the water. This method has the advantage of giving results directly in terms of the calorie as usually defined (p. 9), so that they may immediately be reduced to dynamical measure by means of Rowland's and others' measurements of the dynamical equivalent of heat. On the other hand are the disadvantages well known to affect the measurement of specific heats by the same method, chiefly (1) the difficulty of exact thermometry, the rise of temperature of the water being always small; (2)

the correction for thermal capacity of the calorimeter, thermometer, &c.; (3) the correction for radiation. The way in which these difficulties are met in practice will be seen best from a description of the actual forms of apparatus used for reactions of various types[1].

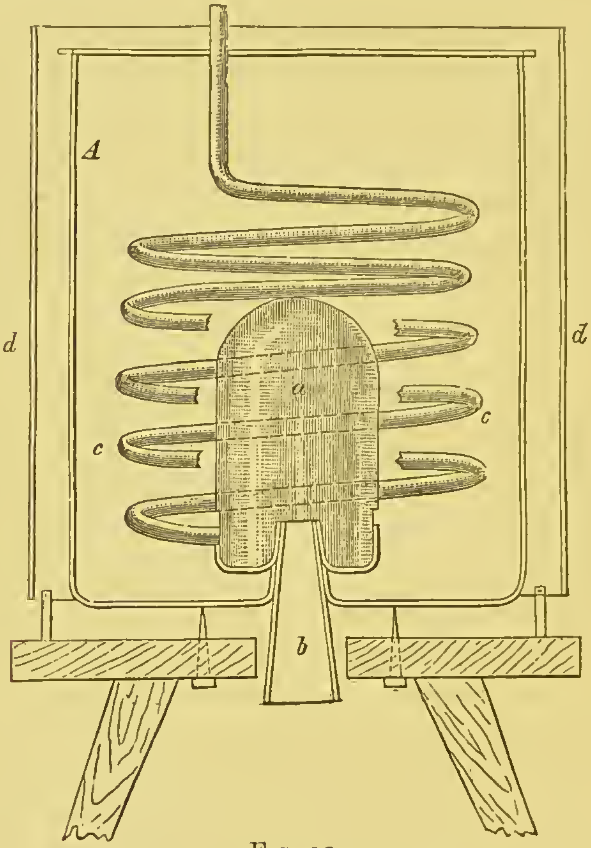

Fig. 32.

To measure the *heat of combustion* of a liquid, Thomsen used the apparatus shown in Fig. 32. A water calorimeter A, protected merely by a metal covering *d*, contains the combustion chamber *a* of 200 c.c. capacity, and the delivery tube *c* in which the products of combustion are cooled, the tube being 180 cm. long and half a centimetre wide. The whole is made of platinum and is provided with a conical tube *b*, into which fits the india-rubber stopper of the burner (Fig. 33). The latter consists of a glass vessel *a* containing liquid to be burnt, a wick by which the vapour is led into the neck *b*, which is surrounded by an electrical heater *d*. By means of the latter heat is supplied for the evaporation, and the flow of vapour can be exactly controlled to give the most convenient flame. If necessary a current of air can be led in through *g* to evaporate the liquid more easily, or a current of hydrogen to make it burn better. The vapour is burnt at the top of the thin platinum tube *h* in an atmosphere of oxygen supplied through *l*. A pair of silver wires hanging from the burner down the tube *b* serve to keep the vapour warm and avoid condensation; while the tube is thermally isolated by being fitted with a cork into the outer tube *k*. The burner is lighted and placed in a glass chamber of the same shape as that of the calorimeter, and then regulated so that the flame is of a reasonable size and free from soot. It is then placed in the calorimeter and the experiment carried out. The products of combustion are drawn away by an aspirator through calcium chloride tubes and potash bulbs, so that they may be estimated

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[1] The following descriptions and results are taken from J. Thomsen, *Thermochemische Untersuchungen* (4 vols.), Leipzig, 1882–86, and Berthelot, *Thermochimie* (2 vols.), Paris, 1898. A valuable summary of results is given in Ostwald's *Lehrbuch* (2nd edit.), vol. 2, part 1, Leipzig, 1893. Reference may also be made to the numerous measurements of Stohmann, *J. f. prakt. Chem.* vol. 31 and onwards.

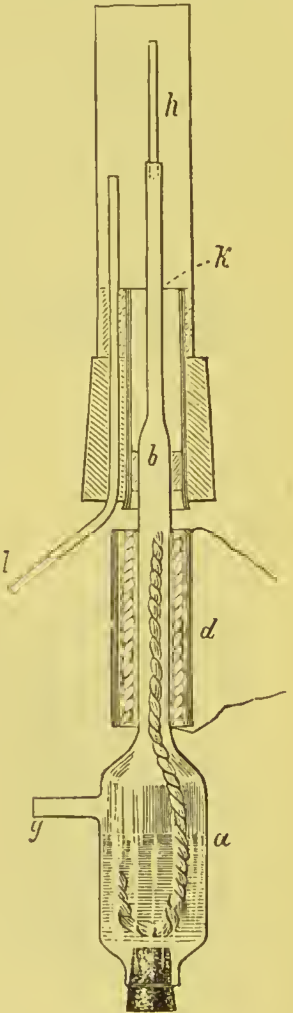

Fig. 33.

in the usual manner of organic analysis, and the weight of liquid burnt may be calculated. Gases may be burnt in the same apparatus, being led in through *g*.

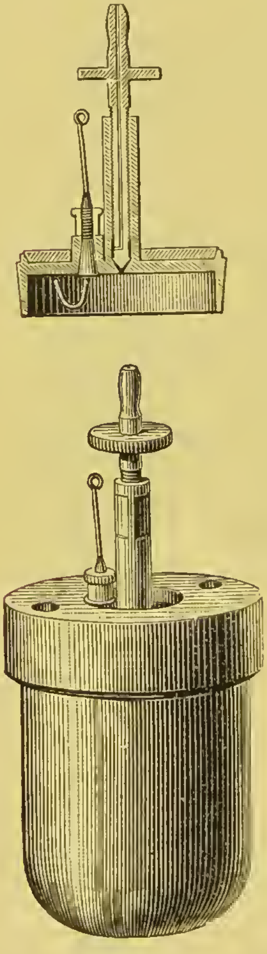

Fig. 34.

An entirely different apparatus, which has received the name of *calorimetric bomb*, has been worked out by Berthelot and his assistants. They found that the combustion of most organic substances is more complete and certain when carried out in oxygen at a moderately high pressure: they then conceived the notion of carrying it out rapidly and in a closed vessel entirely immersed in the calorimeter. The vessel or 'bomb' is a cylinder of steel (Fig. 34) with a lid that screws on air-tight; it is lined internally with platinum so that the substances used do not in any case come into contact with the steel. The substance to be burnt is weighed out and placed in a little platinum capsule, the lid screwed on, and the bomb, which holds about $\frac{1}{4}$ litre, filled with oxygen at 25 atmos. pressure through the tubes provided with a screw tap. The whole is then placed in the calorimeter and ignition produced by a current of electricity which incandesces a wire in contact with the substance. The details of the method of ignition can be modified to suit various cases. A method that is frequently available is to lead the current through an iron wire lying in contact with the organic substance; the wire is burnt, and sets fire to the substance; it is easy to allow for the heat of combustion of the iron. The combustion is very rapid, and four or five minutes suffice to allow the heat to diffuse into the calorimeter, so that the correction for radiation is minimized, and all errors due to uncertainty as to the temperature of the reagents vanish. Experiment shows that the combustion is complete to 1 in 1000. On the other hand, the thermal capacity of the bomb is considerable, being equal to that of 300–400 gms. of water.

For *reactions between liquids* much simpler apparatus suffices, e.g. a pattern described by Nernst[1] (Fig. 35), consisting of a beaker of about 1 litre capacity, isolated and supported by corks inside a larger beaker. The latter has a wooden lid which carries a wide test-tube in which the reaction is carried out, a finely graduated thermometer (conveniently that of a Beckmann freezing-point apparatus), and a simple platinum wire stirrer. The thermal capacity of the calorimeter is somewhat uncertain, from its being made of badly conducting material, but is in any case small compared with that of the water it contains; the radiation correction is negligible because the rise of temperature occurring is only a degree or two, and the reaction is usually very rapid.

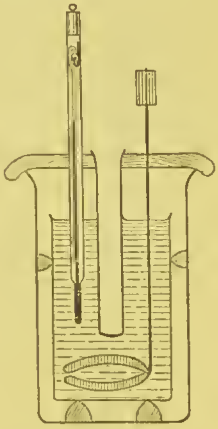

FIG. 35.

When possible it is advantageous to make the reacting liquids themselves serve as calorimetric substance; e.g. this is commonly done in measuring heats of neutralization. A previous knowledge of the thermal capacity of the mixture is of course required; it is then only necessary to observe the temperatures before and after mixing. It is desirable that the two liquids should be as nearly as possible at the same temperature beforehand; this is satisfactorily accomplished in an apparatus designed by Pickering[2]. It consists of a platinum vessel of the shape of an oval cylinder 14 × 8 × 10 cms. deep, divided into two equal parts by a partition of platinum free to rotate round a central pivot and made water-tight by a packing of sheet india-rubber. The liquids to be mixed are put in the two compartments, with a thermometer in each, the whole being enclosed in a water-jacket and provided with stirrers in the usual way. When the temperature of the two solutions is as nearly as possible the same, the partition is rotated so as to mix the two liquids, and the rise of temperature noted; that multiplied by the thermal capacity gives immediately the quantity of heat evolved. It is not necessary to use such expensive and special apparatus, however, as the method has been carried out very successfully by means of a pair of ordinary glass vessels, as e. g. by Berthelot (*loc. cit.*).

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[1] *Ostw.* 2. 23.

[2] *Phil. Mag.* (5) 29. 247.

In the case of salt solutions the calculation is simplified by the somewhat remarkable empirical rule that the *thermal capacity of the solution* is approximately equal to that of the water it contains, alone. Thus $NaNO_3$ dissolved in 200 mols. of H_2O has the specific heat 0·975; this multiplied by the formula weight 85 + 3,600 gives 3,593 as the thermal capacity of that amount of solution expressed by the formula, while the 200 mols. of water alone would have a capacity 3,600, the difference being -7. For 100 H_2O the difference is -9, 50 H_2O $+4$, 25 H_2O $+11·7$, while for other salts the difference is sometimes positive, sometimes negative.

For details of exact thermometry we must refer to treatises on physics, and especially to Guillaume, *Traité pratique de la Thermométrie* (Paris, 1889). It may be pointed out that, to make use of the table of values of the calorie given on p. 9, it is necessary to reduce the thermometer readings to the standard hydrogen scale. The correction for thermal capacity of the calorimeter, &c., is usually estimated from the weight of each substance, platinum of calorimeter, glass and mercury of thermometer, &c., that shares the rise in temperature, and its known specific heat. The *radiation correction* is usually the most uncertain point of the experiment; it may be found approximately as follows:—

Let t_1, t_2 be the temperatures of the calorimeter before and after the reaction, t_0 that of the surroundings (water-jacket, if there is one), then $\frac{(t_1+t_2)}{2}$ may be taken as the average temperature during the experiment, and $\frac{(t_1+t_2)}{2}-t_0$ the excess over surroundings (this quantity should be made as small as possible). Leave the calorimeter to itself, only stirring occasionally, for a time equal to the interval between the observations t_1 and t , suppose the temperature has at the end of that time fallen by radiation to t_3. During this second period the average temperature excess is $\frac{(t_2+t_3)}{2}-t_0$, and since, by Newton's law of cooling, the radiation is proportional to the excess of temperature, we shall have

$$\tau : t_2 - t_3 :: \frac{t_1+t_2}{2} - t_0 : \frac{t_2+t_3}{2} - t_0,$$

where τ is the fall of temperature due to radiation during the experiment. Hence, instead of the observed rise of temperature $t_2 - t_1$, we must take the corrected value

$$t_2 - t_1 + \tau.$$

The *Bunsen calorimeter* possesses the important advantage of being constantly at one temperature, so that no thermometry is involved in its use, and no radiation correction has to be made when the instrument is in proper working order. Actually it is impossible to surround the working part of the apparatus completely with ice at strictly the same temperature as itself, so that there is usually a slight movement of the mercury column when the instrument is not in use; but the correction for this may be made very small, especially if an air-jacket be interposed between the working part and the ice bath, as suggested by Boys. The calorimeter may be employed in the original manner by observing the movement of a thread of mercury in a calibrated capillary tube; this has the advantage of showing the changes progressively; otherwise it is better to determine the contraction of the ice by causing the end of the capillary to dip in a beaker of mercury, and weighing the amount drawn in during an experiment. The Bunsen calorimeter is appropriate for measuring very small quantities of heat. It has, however, been objected to it that the unit in which the heat is measured is not known with sufficient accuracy. If v be the specific volume of ice, v' that of water, l the latent heat of fusion, then when one calorie is imparted to the instrument, the mixture of ice and water contracts by $\frac{v-v'}{l}$ c.c., and if d be the density of mercury, the weight drawn in will be $\frac{v-v'}{l}d$. This quantity may be calculated by observations on the density and latent heat, or may be directly observed by pouring a known weight of warm water into the apparatus. Bunsen found 0·01541 as the weight of mercury per calorie, while the results of other observers have differed by as much as $\frac{1}{250}$ from this. This is greater than the uncertainty existing in the value of the dynamical equivalent of heat, so that the ice calorimeter cannot be regarded as being so accurate as the water calorimeter. It should, however, be possible to obtain the constant of the Bunsen calorimeter directly in dynamical measure by generating a measured quantity of energy electrically in it, and observing the weight of mercury drawn in. Dieterici's[1] experiments conducted in that manner give the constant as 0·01533 grams of mercury per therm. ($4{\cdot}2 \times 10^7$ ergs).

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[1] *Wied.* 33. 417 (1888).

§ 3. Classification of Results.

If we accept the view stated in the preceding chapter, that chemical reaction, even when apparently between different phases, really takes place in a single (fluid) phase between the obviously gaseous (or liquid) constituents and traces of the remaining constituents in the form of vapour (or solution), it follows logically that the thermal changes involved may be classified into (1) latent heat accompanying change of state; (2) heat due to the reaction occurring within a single phase. In the case of an apparently heterogeneous reaction, e. g. solution of a metal in acid, the evolution of heat might be analyzed into those two parts. We cannot always perform the analysis, but it will help to make the subject intelligible to bear the distinction in mind.

We have then in consequence of change of state:

(*a*) Heat of evaporation of a liquid.

(*b*) Heat of sublimation of a solid.

These quantities, so far as is known, are the same whether the evaporation occurs in a vacuum or in presence of other gases or vapours. On the other hand, a considerable amount of external work is done in evaporation, so that in determining the change of internal energy (or internal latent heat, as it is sometimes called) the corresponding correction must be made (examples p. 245).

(*c*) Heat of fusion of a solid.

(*d*) Heat of solution of a solid.

(*e*) Heat of solution of a gas.

By analogy with evaporation these may be taken to mean the heat evolved when one gram-molecule of solid or gas combines with so much solvent as to produce a saturated solution; but the various cases will be treated in detail below.

(*f*) Heat of transition from one solid phase to another.

E. g. transition from rhombic to monosymmetric sulphur.

Further, the heat developed in dissolving a liquid in another which is imperfectly miscible with it, in mixing two completely miscible liquids, and in diluting a solution of a solid or gas, constitute intermediate cases between mere change of state and chemical reaction.

As the thermal phenomena involved in solution are somewhat complex and liable to misunderstanding, we shall treat them in more detail, dealing first with simple solution, and then with complete mixture. If a mol. of the solid B (salt or other substance) be dissolved in x mols. of a solvent A (e. g. water), we may express the *evolution* of heat by

$$[xA,\ B] = q,$$

and describe the quantity as the heat of solution of B. In order to effect the solution a certain minimum amount a of water at least must be used, since the solid is only soluble to a limited extent. The heat of solution in a mols. of water or

$$[aA,\ B] = q_a$$

has been called the *integral heat of solution*; in other words it is the heat of formation of $1+a$ mols. of the saturated solution. When more solvent than this is used, the value of q will be somewhat different (greater or less in particular cases), but as the quantity of solvent is increased indefinitely the evolution of heat tends towards a finite limiting value which is called the *heat of dilute solution*, and may be written

$$[\infty A,\ B] = q_x.$$

These relations are shown in Fig. 36.

If to a solution already containing x mols. of water to 1 of salt x' more of water be added, the evolution of heat is

$$[xA + B,\ x'A] = q_{x+x'} - q_x,$$

and is represented by the difference in height of the ordinates corresponding to x and $x+x'$. For unit addition of water this becomes equal to the tangent of the angle of slope of the curve, and may be called the *heat of dilution*.

[That is, $[xA + B,\ dxA] \div dx = \frac{dq}{dx}$. This quantity varies from a finite value $\left(\frac{dq}{dx}\right)_a$, the *heat of dilution of the saturated solution*, to $\left(\frac{dq}{dx}\right)_\infty = 0$ for the dilute solution.]

Thus e.g. Thomsen found that a solution of the composition $Cu\,Cl_2 + 10\,H_2O$ (nearly saturated) gave, on mixing with further quantities of water, the following liberation of heat (at 18^c):

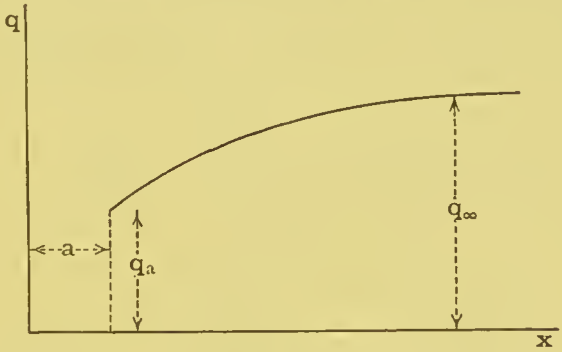

Fig. 36.

Added H_2O .	10	20	40	90	190	$= x'$.
Heat evolved	1606	2430	3308	4052	4510	$= q$.

These numbers are well represented by the expression

$$\frac{x' \times 5023}{x' + 21{\cdot}24};$$

hence we may conclude that on infinite dilution we should get an evolution of 5,023 cal. The heat of solution of the dry salt in 600 mols. $H_2O = 11{,}080$, and the preceding formula indicates that 174 calories would be obtained by diluting the solution in $600\,H_2O$ infinitely further. Hence we get $q_\infty = 11{,}080 + 174 = 11{,}254$ and $q_{10} = 11{,}254 - 5{,}023 = 6{,}231$. The value of a (a little less than 10) and of q_a were not determined.

It is sometimes convenient to express the heat involved in adding a variable quantity of salt (B) to a fixed quantity of solvent (A), i.e.

$$[A,\ yB] = q',$$

where y is the number of mols. of salt for one of solvent; q' is shown graphically by Fig. 37. The value of y must lie between 0 and a fixed value b corresponding to saturation, and clearly for the same solution $y = \frac{1}{x}\cdot$ The limiting value q'_b is the heat of formation of $1+b$ mols. of saturated solution. Hence the *heat of formation* (per mol.) of saturated solution $= \frac{q'_b}{(1+b)} = \frac{q_a}{(1+a)}\cdot$ If to a solution already containing y mols. of salt y' more are added, the evolution of heat is

$$[A+yB,\ y'B] = q'_{y+y'} - q'_y,$$

and is represented by the difference in height of the ordinates corresponding to y and $y+y'$; for unit addition of salt this becomes equal to the tangent of the angle of slope of the curve. The slope of the curve is by no means always similar to that shown in the figure; in many cases the curve while starting upwards bends over to a horizontal direction, or even downwards before coming to an end. The slope at the end expresses the *limiting heat of solution*, i.e. the heat of solution of the last mol. of salt that goes to form an indefinite quantity of the saturated solution; this quantity has been frequently used in thermodynamic reasoning on solutions.

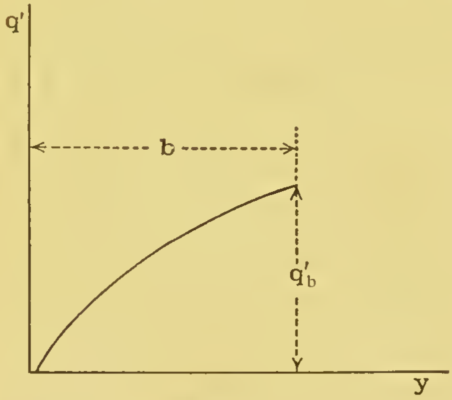

FIG. 37.

[That is, $[A+yB,\ dyB] \div dy = \frac{dq'}{dy}$ is the heat of solution in a solution already containing y mols. of salt, and on reaching saturation this becomes $\left(\frac{dq'}{dy}\right)_b$, the *limiting heat of solution*, a quantity which may differ even in sign from $\left(\frac{dq'}{dy}\right)_0$, the *initial heat of solution*. The relation between these quantities and the preceding is easily found, for $y = \frac{1}{x}$ and $q' = \frac{q}{x}$; hence

$$\frac{dq'}{dy} = \frac{d\left(\frac{q}{x}\right)}{d\left(\frac{1}{x}\right)} = q - x\,\frac{dq}{dx},$$

or at saturation

$$\left(\frac{dq'}{dy}\right)_b + a\left(\frac{dq}{dx}\right)_a = q_a, \text{ or in words],}$$

the integral heat of solution = limiting heat of solution + a times the heat of dilution of the saturated solution; a being the number of mols. of solvent saturated by one mol. of dissolved body.

We may take, as an example of this, Thomsen's measurements on sodium nitrate. The quantity of salt expressed by the formula $Na_2N_2O_6$ takes $a = 10{\cdot}9$ mols. H_2O to dissolve it at 18°; the measurements of the heat of dilution, however, extend only from 12 to 400 mols., and may be represented by

$$q = -5.868 - 4{,}700 \times \frac{x-12}{x+28{\cdot}96},$$

heat being absorbed both on solution and dilution. Assuming this formula to be correct over the whole range of solubility, we have

Heat of dilute solution $q_\infty = -10{,}568$;
Integral heat of solution $q_a = -\;5{,}738$;
Heat of dilution of the saturated solution $\left(\frac{dq}{dx}\right)_a = -121{\cdot}2$;
Limiting heat of solution $q_a - a\left(\frac{dq}{dx}\right)_a = -4417$.

In the *complete mixture* of two liquids the curves corresponding to those in Fig. 36, 37, both extend from 0 to ∞ in the horizontal direction, and become reciprocal to one another. The heat of formation of any mixture may be calculated from either of them, but it is more convenient to draw a curve in which the heat of formation (Q) (i. e. of 1 mol. of solution) is itself taken as ordinate, and accordingly the molecular fractional composition (z) as abscissa, so that the curve is finite in length, extending only from $z=0$ to $z=1$. It has the general shape shown in Fig. 38. The relation between this curve and the preceding ones is given by

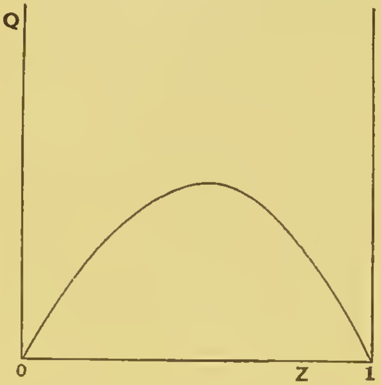

Fig. 38.

$$z=\frac{x}{x+1}=\frac{y}{y+1},$$

$$Q=\frac{q}{x+1}=\frac{q'}{y+1}.$$

The best-known instance of the evolution of heat on mixing two liquids is that of sulphuric acid and water. The observations[1] are fairly represented by J. Thomsen's formula

$$[x\mathrm{H_2O},\ \mathrm{H_2SO_4}]=q_x=\frac{17860x}{x+1{\cdot}7983}.$$

From this we may obtain by the preceding equations the heat of formation of mixtures expressed in terms of their molecular fractional composition z,

$$Q=\frac{z(1-z)}{1-0{\cdot}4439z}\times 9932.$$

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[1] J. Thomsen, l. c.; Pickering, *J. C. S.* 57. 112.

This equation gives the following values, which, it will be seen, correspond with the general character of Fig. 38 :—

Mol. fraction of water (z)	0·2	0·4	0·6	0·8
Heat of formation (Q)	1740	2900	3250	2460

§ 4. Application of the Second Law of Thermodynamics.

We saw in chap. iii that the second law of thermodynamics leads to certain relations between the changes in the state of equilibrium of any system with temperature and the quantities of heat involved in those changes. In particular two such relations are needed for the study of chemical systems, viz. :—

(1) When in a heterogeneous system matter passes from one phase to another, if Q be the latent heat of transition, Δv the increase of volume accompanying the process (at constant temperature), then

$$\frac{Q}{T \times \Delta v} = \frac{\partial_v p}{\partial T},$$

the right-hand side of the equation expressing the rate of increase of pressure of the system per 1° rise of temperature (at constant volume).

(2) When in a homogeneous system which is dilute, so that the law of mass action is applicable to it, a reaction occurs involving an absorption of heat, Q, and K be the reaction constant,

$$\frac{Q}{T} = -RT\frac{\partial_v \log K}{\partial T},$$

the differential coefficient $\frac{\partial_v \log K}{\partial T}$ expressing the rate of increase of the logarithm of the reaction constant per 1° rise of temperature (at constant volume).

These relations have been successfully applied to a large number of actual cases, some of which we proceed to consider.

(*a*) *System of one component: heat of transition in condensed equilibrium.*

The fusion of ice is accompanied by an absorption of 1,440 cals. (per mol.). The temperature of fusion is 273°; the specific volume of ice is 1·0909, that of water 1·0001, so that the increase of volume (per mol.) $= 18\,(1{\cdot}0001 - 1{\cdot}0909) = -1{\cdot}6344$ c.c. We have then

$$\frac{dp}{dT} = -\frac{1{,}440 \times 42{,}000{,}000}{273 \times 1{\cdot}6344} = -136 \times 10^6 \text{ dynes/sq. cm.}$$
$$= -136 \text{ atmos.}$$

The quantity of heat is converted into ergs, so that the result may be expressed in the C.G.S. system. We see that a fall of temperature of 1° is caused by a rise of pressure of 136 atmospheres. W. Thomson found experimentally 130 atmos.—very close agreement, considering the small change of temperature to be measured.

In the transformation of rhombic into monosymmetric sulphur at 95·5°, an absorption of 2·52 calories per gram occurs; the volume increases by 0·0126 c c. per gram, so that

$$\frac{dp}{dT} = \frac{2{\cdot}52 \times 42{,}000{,}000}{(273 + 95{\cdot}5) \times 0{\cdot}0126} = 22{\cdot}8 \times 10^6.$$

Experiments by Reicher gave 21 atmos. (see p. 225).

(*b*) *System of one component: heat of evaporation.*

Evaporation of water at 100°. Regarding Q as the quantity to be determined, we may take from Regnault's observations

$$\frac{dp}{dT} = 27{\cdot}25 \text{ mm. of Hg} = 36{,}330 \text{ dynes/sq. cm.}$$

The specific volume of water is 1, that of saturated steam about 1,654. Hence the latent heat (per gram) is

$$36{,}330 \times 373 \times (1{,}654 - 1) = 2{\cdot}24 \times 10^{10} \text{ ergs} = 533{\cdot}3 \text{ calories,}$$

in very close agreement with the results of direct measurement.

Experimental determination of the density of a saturated vapour is difficult, but in many cases we may obtain sufficiently accurate data by *assuming that the vapour behaves as a perfect gas*, and neglecting the volume of the liquid or solid by comparison with it. We then have for Δv simply the volume of a mol. of vapour according to the gaseous laws, i. e. $= RT/p$. Substituting this value in the general equation, we find

$$Q = \frac{RT^2}{p}\frac{dp}{dT} = RT^2\frac{d\log p}{dT}.$$

In the case of water vapour at 100°, the volume reckoned according to the gaseous laws is 1,701 c.c., so that the equation just given yields a value of Q, that is three per cent. too high; but for low pressures the approximation is much better. The equation, moreover, has the important advantage that it can be integrated directly on the *assumption that Q is constant*, yielding

$$\log_e \frac{p_2}{p_1} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

where p_1 is the vapour pressure corresponding to T_1, p_2 that corresponding to T_2. Heats of reaction, as we have seen, usually vary but little with temperature, so that the assumption is justified; this and other similar expressions may therefore commonly be used to calculate a heat of reaction from two observations a few degrees apart in temperature. The latent heat of evaporation actually diminishes on rise of temperature, tending towards zero at the critical temperature. The equation just given was employed above in calculating the raising of the boiling point by solution (p. 32).

(c) *System of more than one component: heat of transition in condensed equilibrium.*

Heat is always absorbed at the transition point in passing from the system stable at lower to that stable at higher temperature. Hence, as in the case of fusion, a system that expands on transition will suffer transition at a higher temperature the higher the pressure; one that contracts, at a lower temperature. The formula connecting the change of temperature with the expansion or contraction is identical with that for systems of one component. A qualitative confirmation is given by Spring and van 't Hoff[1] for the transition

$$CuCa(C_2H_3O_2)_4 \cdot 6H_2O \rightleftarrows Cu(C_2H_3O_2)_2 \cdot H_2O + Ca(C_2H_3O_2)_2 \cdot H_2O + 4H_2O,$$

which takes place at about 77° under atmospheric pressure and is accompanied by a contraction, the second system occupying a smaller volume than the first. The transition point should accordingly be lowered by pressure, and indeed was found to be about 40° under 6,000 atmospheres.

(d) *More than one component: vapour pressure of dilute systems.*

It will be sufficient to consider a system of two components, the behaviour of the more complex being very similar. Further, we shall confine our attention to the case in which only one component is sensibly volatile, i. e. the familiar case of salt solutions and the like. If three phases exist – salt, saturated solution, and vapour – there is, as we have seen, a vapour-pressure curve similar to that of a simple liquid, the pressure being a function of the temperature only. The rate of change of the pressure constitutes the term $\frac{\partial_{\bar{v}} p}{\partial T}$ in the thermodynamic relation, since, if the system be heated at constant volume, the vapour will remain saturated so long as none of the three phases disappears; it should be noted that the concentration of the solution does not remain constant during the process. In evaluating the left-hand member $\frac{Q}{T \times \Delta v}$ we have to suppose a small increase of volume to be made while the temperature remains constant; this will involve evaporation of some of the water, and, since the solution remains saturated, precipitation of a corresponding amount of salt. For one mol. of salt, a mols. of water are evaporated, and the increase of volume may be reckoned according to the gaseous laws. In order to calculate the absorption of heat we may suppose the process to be divided into two parts: (1) decomposition of $1+a$ mols. of saturated solution; (2) evaporation of the a mols. of pure water separated. (1) is accompanied by an *absorption* of heat identical with the evolution on forming saturated solution q_a; hence, if λ be the molecular latent heat for pure water, the heat of evaporation out of the solution is the sum of these two quantities, or

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[1] *Bull. de l'Acad. Roy. de Belgique*, 49. 344.

$$\lambda + \frac{q_a}{a} = \frac{RT^2}{p} \frac{dp}{dT}.$$

q_a is usually negative, e. g. for $Na_2N_2O_6$ at $18° = -5{,}738$, whilst $a = 10{\cdot}9$. Thus, while $\lambda = 10{,}692$ for water, the corresponding quantity for the solution is $10{,}692 - 5{,}738 \div 10{\cdot}9 = 10{,}166$; hence the vapour pressure of the solution rises more slowly with temperature than that of pure water; for solutions of $CuCl_2$ the reverse is true, since that salt dissolves with evolution of heat (p. 259).

The relation just found illustrates the point mentioned on p. 218, that at a transition point the curve of vapour pressure of the saturated solution shows a sharp bend upwards; for, since the transition is always accompanied by absorption of heat, $\lambda + q_a/a$ must have a larger value above the transition point than below, and the same is consequently true of $\frac{dp}{dT}$.

The same equation is applicable to the vapour pressures of solid hydrates, e. g. the reaction

$$Cu\,SO_4 \,.\, 5H\ O \rightleftarrows Cu\,SO_4 \,.\, 3H_2O + 2H_2O \text{ (gas)}$$

takes place in a system of three phases, so that there is a definite saturation pressure for each temperature. The thermal value of the reaction is, according to J. Thomsen, $-2 \times 10{,}692$ cals. for the evaporation of two mols. of water, $-6{,}820$ cals. for the separation of liquid water from the salt, giving 14,102 per mol. as the latent heat. The vapour pressure, according to Frowein[1], is

2.993 mm. at 13·95°,
5·056 ,, ,, 20·46°,
8.074 ,, ,, 26·30°.

Using the thermodynamic equation in the integral form,

$$\log_e \frac{p_2}{p_1} = \frac{Q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

we get from the observations at 13·95° and 26·30° Q = 13,912 per mol. of H_2O against the calorimetric value 14,102.

If the same reasoning be applied to a system in two phases, viz. unsaturated solution and vapour, it is necessary to introduce some new condition, since the vapour pressure depends now on two independently variable quantities—the temperature and concentration. We shall obtain the most useful results if we set the concentration constant; the rate of change of the vapour pressure is then that expressed by $\frac{\partial_x p}{\partial T}$. Since when evaporation takes place no salt separates out, the heat of evaporation will be the sum of the heat of evaporation of pure water λ and the heat of dilution $\frac{dq}{dx}$, so that

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[1] *Ostw.* 1. 1.

$$\lambda + \frac{dq}{dx} = \frac{RT^2}{p} \frac{\partial_x p}{\partial T}.$$

Now when the solution is already very dilute no heat is evolved on diluting it further, so that $\frac{dq}{dx} = 0$. If the equation be then compared with that for the pure solvent,

$$\lambda = \frac{RT^2}{p} \frac{dp}{dT},$$

we see that the fractional rate of change of the pressure $\frac{dp}{pdT}$ must be the same for both, so that whatever ratio holds between the pressures of the solvent and solution at any temperature will hold at any other temperature (Babo's law). This result is included in Raoult's law of the lowering of vapour pressure (p. 31), in the proof of which it is not merely shown that the relative lowering is constant, but the amount of it was found to be equal to the ratio of the number of molecules of dissolved substance to those of solvent.

(*e*) *More than one component: osmotic pressure of dilute systems.*

In accordance with the analogy between dilute solutions and gases, the same thermodynamic relation may be applied to a solution, osmotic pressure taking the place of gas pressure. We may imagine a system consisting of solid and solution in contact on one side of a semipermeable piston, pure solvent on the other; and the whole in an enclosure of constant volume. There will then be a pressure on the piston tending to move it so as to allow the solvent to flow through into the solution. Calling the osmotic pressure P and volume of the solution V, and introducing the gaseous laws in the thermodynamic relation, the latter becomes

$$Q = RT^2 \frac{d \log P}{dT},$$

where Q is the heat absorbed when one molecule of solid goes into solution.

Under these circumstances the solution does work to the extent RT owing to its increase of volume, whereas if a molecule of solid be dissolved in a calorimeter no work is done, and therefore the absorption of heat is less by RT. But it is the heat absorbed when one molecule is dissolved (to saturation) in a calorimeter that we have designated q_a, so that in the experiment with the semi-permeable piston the absorption must be

$$q_a + RT = RT^2 \frac{d \log P}{dT}.$$

Instead of the osmotic pressure it is more convenient to work with the concentration of the solid in solution C. Since $P = RTC$ and R is a constant, we have

$$q_a + RT = RT^2 \frac{d(\log C + \log T)}{dT} = RT^2 \frac{d \log C}{dT} + RT,$$

or simply

$$q_a = RT^2 \frac{d \log C}{dT},$$

so that the integral heat of solution as ordinarily measured is proportional to the fractional rate of change of the *concentration.* In its integrated form this equation becomes

$$\log_e \frac{C_2}{C_1} = \frac{q_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

on the usual assumption that the variation of q_a with temperature may be neglected. This result was arrived at by van 't Hoff[1], who gives the following table of experimental verification. Only solutions of (practically) non-electrolytes are referred to, in order to avoid the complication due to electrolytic dissociation.

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[1] *Kongl. Svenska. Akad. Handl.*, 1886, p. 38.

	C_1.	T_1.	C_2.	T_2.	q_a (*calc.*).	q_a (*obs.*).
Succinic acid .	2·88	0°	4·22	8·5°	6900	6700
Benzoic acid .	0·1823	4·5	2·1931	75	6700	6500
Salicylic acid .	0·16	12·5	2·44	81	9000	8500
Boric acid . .	1·947	0	2·92	12	5200	5600
Phenol . . .	7·12	1	10·2	45	1200	2100
Mercuric chloride	6·57	10	11·84	50	2700	3000

If the dissolved substance be an electrolyte, the relations of concentration and evolution of heat are complicated by the fact that as the concentration changes, the degree of dissociation does so too. We shall not consider this case in general, but when the dissociation is so great that it may practically be regarded as complete for all strengths of solution that occur, the treatment again becomes simple. This state of things holds for nearly insoluble salts such as $\mathrm{Ba\,SO_4}$ and $\mathrm{Ag\,Cl}$. We have then, if ι be the number of ions formed from a molecule of the salt, that the osmotic pressure $P = RT\iota C$, where C is taken as before to mean the concentration expressed in terms of the ordinary formula for the salt. We have, therefore, only to introduce ι into the thermodynamic relation, which becomes

$$\log_e \frac{C_2}{C_1} = \frac{q_a}{R\iota}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

In this equation the concentrations, referring to saturated solution, may be measured by means of the electric conductivity, since the partial conductivities of the ions are already known. q_a, the heat of solution of the salt (including its heat of dissociation), is the same as the heat of precipitation with reversed sign; for if we mix two neutral salts, say $\mathrm{Ba\,Cl_2}$ and $\mathrm{Na_2\,SO_4}$, in dilute solution, the reaction, bearing in mind the dissociation, is

$$\mathrm{Ba}^{\cdot\cdot} + 2\,\mathrm{Cl}' + 2\,\mathrm{Na}^{\cdot} + \mathrm{SO_4}'' = 2\,\mathrm{Na}^{\cdot} + 2\,\mathrm{Cl}' + \mathrm{Ba\,SO_4},$$

or simply

$$\mathrm{Ba}^{\cdot\cdot} + \mathrm{SO_4}'' = \mathrm{BaSO_4}.$$

The heat of precipitation is thus numerically equal to q_a, and may be measured calorimetrically. The following results have been obtained :—

Salt.	*Temp.*	*V.*	q_a *(calc.).*	q_a *(obs.).*
$BaSO_4$	18·4°	50055	5500	5583
,,	37·7°	37282		
AgCl	13·8°	102710	15992	15850
,,	26·5°	55120		

V is the dilution in litres per gm. mol., so that $C = \frac{1}{V}$.

(*f*) *Homogeneous equilibrium.*

In this case the thermodynamic equation takes, we have seen, the form of a relation between the heat of reaction and the temperature variation of the reaction constant, viz. :—

$$Q = RT^2 \frac{d \log K}{dT}.$$

This equation, in obtaining which the gaseous laws are assumed to hold, is very similar in form to the corresponding equation with regard to change of state when the same assumption is made.

Like the other, this equation may be integrated on the assumption that Q is constant, and gives

$$Q = R \frac{T_1 T_2}{T_2 - T_1} \log \frac{K_2}{K_1}.$$

As an example of the application to gases, we may take the dissociation of N_2O_4. The degree of dissociation has been found under atmospheric pressure as $\gamma = 0{\cdot}1996$ at 26·7°, and $\gamma = 0{\cdot}9267$ at 111·3°. The reaction constant at these temperatures may be calculated, since

$$K = \frac{\gamma^2}{(1-\gamma)v}, \text{ where } v = RT\frac{(1+\gamma)}{p}$$

is the volume containing 92 grams of the peroxide, these constituting $1 + \gamma$ molecules. If the values of $K_1 K_2$ so found be introduced into the equation, we get $Q = 12{,}900$.

On the other hand, the calorimetric measurements of Berthelot and Ogier allow of calculating *Q*; they found that between 27° and 150° the absorption of heat by 92 grams of the gas was 12,620 calories. Of this amount it may be reckoned[1] that a part is spent in actual increase of temperature energy; the molecular specific heat of the peroxide at high temperatures is 16·86 (per 92 grams): we may therefore set this part as $16{\cdot}86\ (150-27) = 2{,}074$. Next, a part is absorbed in doing external work. Now the degree of dissociation is about 0·2015 at the low temperature, 1·0 at the high, i.e. the dissociation is then complete; hence the work done $= 0{\cdot}7985 \times RT = 577$ calories. The remainder of the observed absorption of heat serves for the dissociation of 0·7985 of the gas, whence it follows that the total heat of dissociation is 12,500.

The formation of ethyl acetate according to the equation

$$CH_3COOH + CH_3CH_2OH \rightleftarrows CH_3COOCH_2CH_3 + H_2O$$

offers an instance of the application of the thermodynamic equation to liquids. It is found that the heat of combustion of ethyl acetate is almost identical with the sum of the heats of combustion of the alcohol and acid, so that the reaction expressed by the equation is practically unaccompanied by liberation of heat, or $Q = 0$. In accordance with this it has been found that the reaction constant is very nearly the same at 220° as at atmospheric temperature; both the partial reactions are, of course, accelerated by heat, but each to the same extent, so that the state of equilibrium is unaffected.

The specially important case of neutralization has been successfully treated from the thermodynamic point of view. A typical reaction between a strong acid and strong base may be expressed in terms of the electrolytic dissociation theory as

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + H_2O,$$

---

[1] Van 't Hoff, *Studies in Chemical Dynamics*, 1896, p. 154.

or simply

$$H^{\cdot} + OH' = H_2O,$$

being nothing more than the formation of water from its ions. The evolution of heat on neutralizing any strong base with any strong acid should therefore be the same, and has in fact been found by J. Thomsen to be about 13,680 calories at 25°. It should, however, be possible to calculate this from the dissociation constant of water, according to the equation

$$Q = R\frac{T_1T_2}{T_2 - T_1}\log\frac{K_2}{K_1}\cdot$$

The value of K, from measurements of conductivity, is at

$T =$	0°	2°	10°	18°	26°	34°	42°	50°	
$K =$	0·122	0·152	0·314	0·64	1·188	2·161	3·725	6·150	$\times 10^{-20}$

whence we find from the observations at

0° and 50°	$Q_{25} = 13{,}810$;
2° and 42°	$Q_{22} = 13{,}850$,
10° and 34°	$Q_{22} = 13{,}970$,
18° and 26°	$Q_{22} = 13{,}460$,

a remarkably accurate confirmation of the theory.

A further instance of the use of the thermodynamic relation is in the electrolytic dissociation of weak acids (or bases). The dissociation constants of some acids have been measured (by the method of electric conductivity) over a range of temperature; hence the heat of dissociation may be calculated by the usual equation. E. g. we have

	K *at* 10°.	*at* 40°.	Q (*calc.*).
Acetic acid .	$17{\cdot}9 \times 10^{-9}$	$18{\cdot}7 \times 10^{-9}$	+257
Propionic acid	13·8	14·1	+126
Butyric acid .	16·6	16·2	−144

Q here is the heat absorbed when a molecule of acid is dissociated (without doing external work) into its ions, at the mean temperature considered, viz. 25°.

This quantity may be determined calorimetrically by means of the heat of neutralization of the acid by a strong base. If e. g. acetic acid be mixed with soda, the reaction is essentially

$$C_2H_4O_2 + OH' = C_2H_3O_2' + H_2O,$$

since the soda beforehand, and sodium acetate after, may be looked upon as completely dissociated, while the acid is so hardly at all. The reaction may then be treated as the sum of two: (*a*) dissociation of $C_2H_4O_2$ into its ions; (*b*) combination of H and OH to form water. The thermal value of the latter is, we have seen, 13,680 cals.; that of the former may accordingly be found by difference from the observed heat of neutralization as follows:—

	Heat of neutralization.	*Q.*
Acetic acid .	13,400	+ 280
Propionic acid	13,480	+ 200
Butyric acid .	13,800	− 120

Since *Q* is here found as the difference between two much larger quantities it is much exposed to experimental errors, and the agreement with the values calculated from the dissociation constant must be regarded as very good.

CHAPTER VII

ELECTRO-CHEMISTRY

§ 1. Origin of Electromotive Force.

In the production of an electric current, two factors have to be taken into account—the electromotive force, and the resistance of the circuit round which the current is to flow. Of these, electromotive force (e. m. f. or potential difference) plays the part of a 'moving force' or tendency to make current flow; and the current actually produced is given by the ratio of the e. m. f. to the resistance opposing it (Ohm's law). So far we have paid attention only to one of these factors—resistance, or its reciprocal, conductance—and that merely for the light it throws on the dissociation of electrolytes. There is, however, a more intimate and essential relation between electrical and chemical phenomena, for the passage of an electric current is, in electrolytes, associated with chemical reaction, and the strength of current may be taken as measure of the velocity of reaction. Accordingly we have in the action of a galvanic cell a case in which velocity of reaction may be referred to the two causes, 'moving force' or *affinity*, and *resistance* to be overcome. The velocity of a reaction may always be looked upon as due to two such factors, but in cases other than electrical it is not so easy to see in what way the moving force and the resistance may be defined; hence study of the electrical phenomenon leads to more definite views as to the nature of what may be described as the affinity causing a chemical change. The recent development of electro-chemistry consists chiefly in a study of the causes of electromotive force in galvanic cells: and that development we shall proceed to consider.

Electromotive force occurs at the surface of contact of dissimilar conducting materials, either (1) between two metals, (2) between two solutions, (3) between a metal and a solution. Of these three the first is always very small, and will not be considered in this book, since it is not associated with chemical change; the second is small in amount; it usually occurs in galvanic cells, but may in most cases be ignored by comparison with the third cause of e. m. f., which is much the largest. *A galvanic cell is a combination of two such junctions of metal and solution*; it, as a whole, possesses an e. m. f. which is the sum of those produced at the two surfaces of contact (with their appropriate signs): if the two metals are identical, and also the two solutions, we have a combination in which the two e. m. f.'s exactly neutralize one another (being in opposite senses) and which is therefore devoid of external electromotive force: this is the 'electrolytic cell' referred to in chap. i, e. g. a pair of copper electrodes dipping in copper sulphate solution. A working galvanic cell may be made by choosing either (1) two dissimilar metals, or (2) two dissimilar solutions, or both. Again, the dissimilarity causing e. m. f. may be either (*a*) in chemical nature, or (*b*) in concentration. Thus the primitive volta cell consists of plates of Zn and Ag dipping in dilute H_2SO_4: here the liquid round the anode is identical with that round the cathode, and the electromotive force is due to the dissimilarity in chemical action between the two metals: this therefore belongs to the class of *chemical cells*. But a cell may be made by the combination Zn, concentrated $ZnSO_4$ solution, dilute $ZnSO_4$ solution, Zn. Here the metals are identical, and the electromotive force is due to the tendency towards equalization of concentration between the two solutions; such *concentration cells* are not used for practical production of current, but study of them has done much to elucidate the mechanism of electrical action.

§ 2. Measurement of Electromotive Force.

To measure the e. m. f. of a cell, the arrangement known as the *potentiometer* or 'Poggendorff's compensation method' is adopted. The apparatus is shown in Fig. 39, and consists of the following parts: A is a source of current; it is essential that this should have an electromotive force higher than that of the cell to be measured, and which remains perfectly constant during the measurements. These conditions are satisfied by using two (or sometimes one) storage cells: if these are not to be had, two or three Daniells will serve. *lxm* is a wire through which the current from A flows: its total resistance must remain constant. This may be accomplished by using a pair of resistance boxes for *lx* and *xm*, taking care that when the resistance of the one is increased by taking out plugs, that of the other is decreased by the same amount; but usually *lxm* consists of a uniform fine wire one or two metres long stretched over a scale, similar to that used for measuring electrolyte resistances (p. 63). *x* is a sliding contact-maker, putting any part of the wire *lxm* in connexion with B, the cell

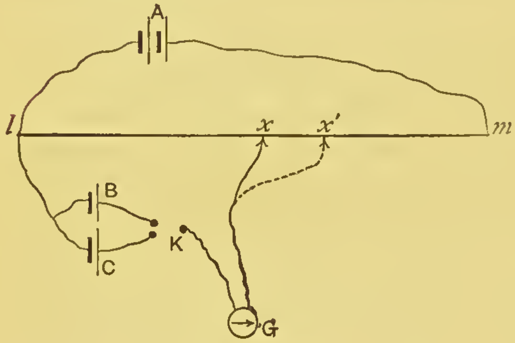

Fig. 39.

to be measured, and C, a cell of known e. m. f. C is usually a Clark cell whose e. m. f. is given by the expression $1{\cdot}434 - 0{\cdot}001\ (t - 15^\circ)$ volts, where t is the temperature. A, B, and C must be arranged so that their like poles are all connected to the same point l. K is a switch by means of which either B or C may be connected to the current indicator G. The latter is not required to measure current, but, as in Wheatstone's bridge, only to indicate when the condition of balance is arrived at, and no current flows through G. As a current indicator it is customary in some laboratories to use a simple form of the Lippmann capillary electrometer (see below, and for practical details see Ostwald, *Handbook of Physico-chemical Measurements*); a mirror galvanometer is, however, perfectly satisfactory and perhaps easier to work with. The whole apparatus may conveniently take the form of a 'Crompton potentiometer,' in which the wire lxm and the key are arranged together on a board, provided with appropriate binding screws for A, B, C, and G; the length of the wire lxm being made alterable, so that when a pair of accumulators is used for A, their electromotive force may be reduced to one volt per metre of wire, by a simple adjustment before the measurements begin; the e. m. f. of the experimental cell may then be read off the scale in decimals of a volt.

To use the apparatus, K is first switched over so as to put the Clark into circuit, and the sliding contact-maker moved till G indicates that no current is flowing through the branch l C G x; when this is the case the e. m. f. of C is just balanced by that existing in the wire between l and x. (In the Crompton pattern the contact-maker is put at 1·434 metres or a neighbouring point, according to the temperature of the Clark cell, and the total length of the potentiometer wire adjusted till no current flows through G.) The switch is then put over to B, and the contact-maker moved till balance is again obtained at some point x'. Since the wire *lxm* is uniform, the e. m. f. between two points of it is proportional to the distance between them ; hence we have

$$\frac{\text{e. m. f. of B}}{\text{e. m. f. of C}} = \frac{\text{length } lx'}{\text{length } lx}.$$

§ 3. Electromotive Force at a Single Contact.

Measurements of electromotive force are necessarily made on complete galvanic cells with two metallic terminals, but to study the relations between e. m. f. and chemical action it is necessary to be able to separate the parts of the e. m. f. due to each metallic contact. This has only been accomplished of late years, and until it was done no considerable progress in electro-chemistry could take place ; in order to measure the e. m. f. at one electrode it is necessary to connect the solution with the galvanometer by another electrode which does not introduce an electromotive force, or else to employ a second electrode whose e. m. f. is known. Two ways of solving the problem have been discovered, viz. (1) by Lippmann's capillary electrometer, (2) by dropping electrodes.

When mercury and an electrolyte—say, dilute H_2SO_4—are in contact in a capillary tube, the level of the mercury is depressed below the level it would occupy in a large vessel communicating, on account of surface tension. There is, however, a difference of potential between the metal and solution, the metal being positively electrified : we may look upon the layers of metal and of acid next the surface of separation as constituting the plates of a condenser, the metal having a positive charge, the electrolyte a negative one. If now a negative charge be imparted to the metal by means of a battery, its potential may be reduced to that of the acid, or even below it. It is found that the surface tension is reduced by electrification, consequently when a negative charge is imparted to the mercury, the effect will be, first, to increase the surface tension, until when metal and acid are at the same potential the surface tension is a maximum: if the charge be further increased, a difference of potential will again be set up—now in the opposite sense—and the surface tension will fall. The experiment can be realized by placing mercury in a dish, covering it with dilute acid, and arranging the end of a capillary tube, also connected with a vessel of mercury to dip in the acid; by suitably adjusting the pressure of mercury in the tube, the surface of contact with the acid may be brought to any desired point of the capillary. If now the mercury in the dish be connected with the positive end of a battery, that in the tube with the negative end, a change of level in the capillary occurs; and by adjusting the e. m. f. applied, the greatest value of the surface tension may be reached: the acid and mercury have then the same potential. Since, however, the surface tension, regarded as a function of the potential applied, is a maximum, a small change in the potential will make hardly any difference to the surface tension, so that the method, though practicable, is not very exact. (Cf. problem of finding the critical volume, p. 89.)

The method of the dropping electrode is not exposed to the same objection. A *dropping electrode* was first used by Lord Kelvin to determine the potential of the air: he allowed water to fall in drops from a funnel made of conducting material; any charge produced in the water by contact with air is carried off by the drops, leaving the mass of water in the funnel at the same potential as the air surrounding it. It was pointed out by Helmholtz that the same principle might be applied to obtain a mass of metal (mercury) at the same potential as an electrolyte. When a fine stream of mercury comes in contact with an electrolyte, the surface of contact tends to become charged—the Hg positively, the solution negatively; but the charge takes an appreciable time to accumulate, since it is necessarily accompanied by a movement of charged ions from the solution. If the stream breaks up into drops they will carry away with them whatever positive electricity is produced on them, leaving the mass of the mercury uncharged. Ostwald[1] realized this condition after many attempts, though still in an imperfect manner, by using a very high pressure of mercury, and as fine drops as possible. Paschen[2], however, showed that the experiment became successful if the mercury was allowed as little time as possible to get charged by contact with the acid; for this reason he raised the vessel of acid until its surface touched the stream of mercury only just above the point at which it broke up into drops. A Hg-pressure of about 200 cms. was used, the metal flowing out through an opening (in a glass tube) of $\frac{1}{20}$ to $\frac{1}{50}$ mm. Under these circumstances the mercury forms a stream of 2 to 10 mm. length before breaking up into drops. If then the level of acid be adjusted correctly, and an electrode of metal M be dipped into the acid, the e. m. f. between M and the Hg of the funnel depends on the contacts Hg: electrolyte, and electrolyte: M. The former, however, produces no e. m. f. in the dropping electrode, so that the measurement gives directly the value of electrolyte: M. It is not, however, necessary to use the troublesome dropping electrode each time it is desired to measure a single e. m. f.; for if the e. m. f. of any single contact be determined as described above, that contact may be combined with the one to be studied, so as to form a cell; we may then measure the e. m. f. of this cell and deduct the part due to the known contact. For this purpose a calomel electrode may advantageously be used, consisting of

$$\mathrm{Hg} : \mathrm{Hg_2Cl_2} : \text{normal } \mathrm{KCl};$$

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[1] *Ostw.* 1. 583–610 (1887).

[2] *Wied.* 41. 42–70 (1890).

the e. m. f. is $-0{\cdot}560$ volt, the mercury being positive to the solution. It is commonly constructed as shown in Fig. 40. Pure mercury is poured into the bottom of a small glass jar, just covered with a little calomel, and the jar filled up completely with normal KCl solution; a rubber stopper is inserted, carrying two tubes: that on the left has a platinum wire sealed through the end, to make contact with the mercury: the other is bent at right angles and leads through a rubber tube to a short hook-shaped glass tube, the whole being filled with the normal KCl solution. If it be desired to measure the e. m. f. at the surface of a metal and electrolyte, these are arranged in any convenient manner, say by immersing a wire of the metal in a beaker of the electrolyte, and the hook-shaped tube dipped into the beaker, care being taken that no air-bubble occurs in the tube. The e. m. f. of the cell so constructed is taken, and that of the normal electrode deducted. E. g. the combination

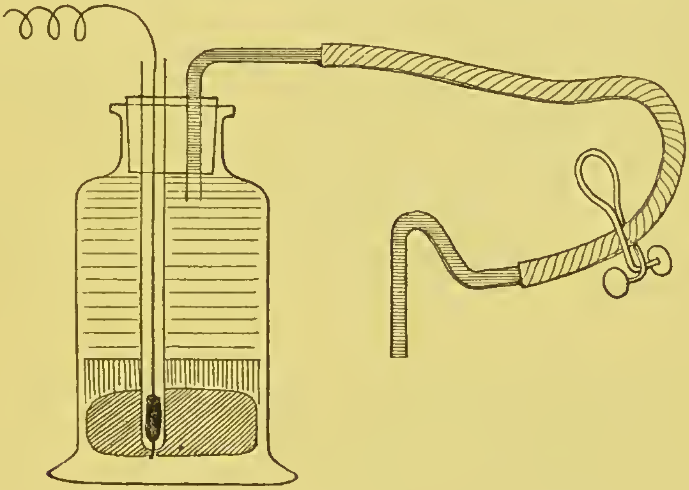

Fig. 40.

$$\text{Cu} : \tfrac{1}{1} \text{ normal } \text{CuSO}_4 : \text{normal electrode}$$

gives an e. m. f. $-0{\cdot}025$, the copper being positive to the mercury. Neglecting the potential difference at the contact of the two electrolytes, the $Cu\,SO_4$ may be taken as at the potential $+0{\cdot}560$. The difference between this and $-0{\cdot}025$ $= 0{\cdot}585$ is the e. m. f. of the combination Cu : $\frac{1}{1}$ norm. $Cu\,SO_4$, the copper being positive. This may conveniently be written

$$\text{Cu} : \tfrac{1}{1}\ \text{norm.}\ Cu\,SO_4 = -0{\cdot}585,$$

the negative sign being taken to mean a step down in potential in passing from the first to the second of the substances mentioned.

Again, the combination

$$\text{Zn} : \tfrac{1}{1}\ \text{norm.}\ Zn\,SO_4 : \text{normal electrode} = +1{\cdot}080,$$

i. e. the mercury of the normal electrode is 1·08 volts positive to the zinc. Hence

$$\text{Zn} : \tfrac{1}{1}\ \text{norm.}\ Zn\,SO_4 = +0{\cdot}520,$$

there being a step up in potential in passing from zinc to zinc sulphate.

§ 4. Electromotive Force of Reversible Electrodes.

The most important distinction to note in the behaviour of various electrodes, is between *polarizable and non-polarizable*. Considering first the behaviour of an electrode with respect to the kation only, it is usually non-polarizable if the solution contains an appreciable quantity of the metal which forms the electrode; e. g. a copper plate immersed in $Cu\,SO_4$ solution is non-polarizable, because it is *reversible* with respect to the kation — Cu. If current flow through it from solution to metal, copper is deposited on the plate; if the current be reversed, copper is dissolved off the plate and goes into solution again; and if the same quantity of electricity has passed in each sense, then, in accordance with Faraday's law (p. 56), the original condition is exactly restored. The e. m. f of the contact is, in such a case, the same whichever way the current flows, and if the concentration of the solution be kept constant, is strictly constant too. On the other hand, if a platinum plate be immersed in dilute sulphuric acid, the solution does not contain platinum (at least not in measurable quantity), and when a current is passed from solution to metal the first effect is to liberate hydrogen on the plate; this dissolves to a certain extent in the platinum, and alters its electrical properties, making its potential much less positive to the solution. When, however, the current is reversed, oxygen instead of hydrogen is liberated on the plate, and the metal is made more positive towards the solution than in its original state. The e. m. f. of the contact is therefore different, according to the direction in which the current flows. The alteration in properties of the electrode, due to the passage of electricity, is known as polarization. As the quantity of electricity, starting from the neutral condition, is increased, the polarization increases in the sense which opposes the applied e. m. f., until a limit is reached at which the metal is saturated with oxygen or hydrogen, and the liberated element begins to appear as a gas; thereafter the e. m. f. is constant, but obviously some of the applied electrical energy is spent in the evolution of gas, which passes away from the cell, so that reversal of the current will not restore the original conditions. Such an electrode is therefore polarizable, and *irreversible* (in the thermodynamic sense).

An electrode may also be made *reversible with respect to the anion*; but, since the materials that contain the anion in the solid state are usually bad conductors of electricity, they must be combined with a metal. E.g. the normal calomel electrode already mentioned belongs to this class; the KCl solution serves essentially as a solution of the anion, Cl, it being immaterial what the metal in solution is. The electrode is essentially the solid Hg_2Cl_2, but it is used in the form of a thin layer in contact with metallic mercury, on account of the better conductivity of the latter. Chlorine passes reversibly between the solution and the electrode, Hg_2Cl_2 being formed or decomposed as the case may be. Similar electrodes can be made with other insoluble salts, such as $AgCl$, $AgBr$, AgI in conjunction with metallic silver, Ag_2S in a solution of KHS, and so on, and also by saturating platinum black with oxygen.

The e. m. f. of reversible metallic electrodes has been measured by B. Neumann[1]. It appears to depend, in the absence of secondary effects, only on the nature of the metal, and the concentration of the ions of that metal in solution. To show this, Neumann made up cells of the pattern

$$Tl : TlCl : \text{normal electrode},$$

using some twenty different salts (organic and inorganic) of thallium, all in centinormal solution. Since in a solution so dilute the salt is practically completely dissociated, the e. m. f. should be the same in all the cells, and that was found to be the case. Nitrates, however, behave in many cases in an anomalous manner, on account of the action of the NO_3 ion on metals: and to avoid such an effect Neumann added urea to the solution, when the e. m. f. became normal.

Cells were constructed with twenty-one different metals in solutions of their salts, made up in each case with the normal calomel electrode; in that way the actual potential differences for the various metals were obtained. Of the metals, however, Mg, Al, and Mn decompose water, with the consequence that the e. m. f. of the cell fell off immediately on immersing the electrode, so that the numbers obtained do not correctly represent the behaviour of the metal. Again, Bi, As, Sb, and Sn form basic salts, so that the true concentration of the solution was not known. The other metals gave the results shown in the following table (nitrates omitted on account of disturbing secondary actions):—

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[1] *Ostw.* 14. 193–230 (1894).

	Sulphate.	*Chloride.*	*Acetate.*
Zinc . .	−0·524	−0·503	−0·522
Cadmium	0·162	0·174	—
Thallium.	0·114	0·151	—
Iron . .	0·093	0·087	—
Cobalt. .	+0·019	+0·015	+0·004
Nickel. .	0·022	0·020	—
Lead . .	—	0·095	0·079
Hydrogen	0·238	0·249	0·150
Copper .	0·515	—	0·580
Mercury .	0·980	—	—
Silver . .	0·974	—	0·991
Palladium	—	1·066	—
Platinum	—	1·140	—
Gold . .	—	1·356	—

The solutions were normal: the + sign indicates that the metal is positive to the solution. Most of the salts are dissociated to the extent of about 40 per cent., so that the concentration of the metallic ions in solution is about 1 gram ion per 2,500 c.c. This is not true, however, for gold and platinum, as the compounds $HAu\,Cl_4$, $H_2Pt\,Cl_6$ are formed in solution, and the concentrations of the ions $Au^{\cdot\cdot\cdot}$ and $Pt^{\cdot\cdot\cdot\cdot}$ are not known; the numbers for these two metals are therefore not directly comparable with the others.

§ 5. Concentration Cells.

The electromotive force between a metal and an electrolyte depends on the concentration of the latter, and, so far as the conception is applicable, on the concentration of the metal too. The possibility of concentration cells was first pointed out by Helmholtz, as a consequence of thermodynamic reasoning which we shall have to consider in more detail below. Briefly, however, it amounts to showing that any work which the materials of the cell can perform in consequence of differences of concentration, may be made available for producing an electric current. *The e. m. f. of the cell may be calculated by equating the electric energy evolved (volts × coulombs) against the osmotic work the materials are capable of doing.* To see how this is so, we will consider in detail a practical case, and for simplicity one in which the ions are univalent, viz. the cell

$$Ag : AgNO_3 \text{ (concentrated)} : AgNO_3 \text{ (dilute)} : Ag.$$

Let C_1, C_2 be the concentrations of the two solutions, of which C_1 is the greater; and let there be a considerable mass of each solution, so that the transfer of a small quantity of salt from one side to the other makes but a trifling difference to the concentrations. Consider what effect on the solutions is produced when unit quantity (1 coulomb) of electricity flows through the cell from right to left, the Ag in the dilute solution being, therefore, the anode; and first assume that the velocities of the anion and kation are the same, which is nearly true for $Ag^{\cdot}$ and NO_3'. Then $\frac{1}{\epsilon}$ gram-atoms of silver go into solution at the anode, where $\epsilon = 96{,}540$ (coulombs per mol.) $\frac{1}{\epsilon}$ gram-atoms of silver are deposited on the cathode, and at the boundary of the two liquids $\frac{1}{2\epsilon}$ of $Ag^{\cdot}$ travels with the current from anode vessel to cathode vessel, the same quantity of NO_3' being transferred in the opposite direction. On the whole, therefore, $\frac{1}{2\epsilon}$ mols. of silver nitrate are gained by the anode solution (dilute), and the same amount lost by the cathode solution (concentrated), so that the two solutions tend to equality. If E be the e. m. f. of the cell, the electrical energy produced (volts × coulombs) is in this case numerically equal to E.

Now the change of concentration might be accomplished by taking out a quantity of the stronger solution containing

$\frac{1}{2\epsilon}$ mols., diluting it down to the strength of the weaker, and then mixing it with that. In order to find how much work could be done by the solution in this process, we must perform it in a (thermodynamically) reversible manner with the aid of a semi-permeable membrane. Let the quantity of solution to be diluted be enclosed in a cylinder with a piston, the base of the cylinder being permeable to water but not to salt, and let the cylinder be placed in water; then the osmotic pressure will cause water to flow into the cylinder and the piston to rise. An amount of work can be done by the piston which is identical with that done by a gas in expanding through the same range of volume; this has been calculated (p. 131), and we may directly apply the result. Assuming the salt to be completely dissociated in solution, the $\frac{1}{2\epsilon}$ mols. become $\frac{1}{\epsilon}$ gram ions, and the work done in dilution is

$$\frac{1}{\epsilon} RT \log_e \frac{C_1}{C_2}.$$

In accordance with the principle quoted at the beginning of the paragraph, this is the e. m. f. of the cell. For R we must take the value expressed in joules (since volt × coulomb = joule), i. e. 8·3157. If the standard temperature of 18° (291° Abs.) be adopted for T, we get

$$E = \frac{8{\cdot}3157 \times 291}{96540} \log_e \frac{C_1}{C_2} = \frac{8{\cdot}3157 \times 291 \times 2{\cdot}3026}{96540} \log_{10} \frac{C_1}{C_2}$$

$$= 0{\cdot}05785 \log_{10} \frac{C_1}{C_2}.$$

Accordingly *for a concentration cell of ratio* 10 : 1 *the e. m. f. is* 0·05785 *volt* (the ions being univalent and of the same mobility, and the salt completely dissociated).

If the ions do not possess the same mobility, but x be the transference ratio for the kation ($1-x$ for the anion), then the anode solution will gain $1-x$ mols. of salt, and the cathode lose the same amount (p. 71). The preceding equation therefore becomes

$$E = \frac{2(1-x)}{\epsilon} RT \log \frac{C_1}{C_2}.$$

Thus Nernst[1] measured the e. m. f. of a cell containing deci- and centi-normal silver nitrate solutions, and found it to be 0·055 volt at 18°. Since in this case $x = 0·52$, the calculated e. m. f. is 0·060; the small difference is accounted for by Nernst by the fact that $AgNO_3$ is incompletely dissociated, and therefore the decinormal solution really contains less than ten times as many Ag *ions* as the centinormal.

Another kind of concentration cell may be made by choosing electrodes of the same material, but in varying concentration; this can be done when the electrode substance is in a state of solution, and two instances of it occur in practice—(1) solutions of solid metals in mercury; (2) solutions of hydrogen in platinum or palladium.

When two dilute amalgams of the same metal are used as electrodes, it is easy to calculate the electromotive force from the change of osmotic energy; for the passage of one coulomb transfers $\frac{1}{\epsilon}$ gram equivalents of the metal from the anode to the cathode, increasing the osmotic pressure of the latter. We may again make use of the principle, that the action of the cell tends to equalize the concentrations, to find its polarity; the anode is clearly the more concentrated. Accordingly to restore the original conditions some of the cathode amalgam must be separated and concentrated till of the same strength as the anode. The $\frac{1}{\epsilon}$ equivalents to be transferred constitute $\frac{1}{r\epsilon}$ gram atoms if r be the valency of the atom (since each valency carries the unit electric charge), and if the metal is monatomic in Hg solution, the same number of gram-molecules. Hence the osmotic work to be done is

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[1] *Ostw.* 7. 477-484 (1891).

$$\frac{RT}{r\epsilon}\log_e\frac{C_1}{C_2},$$

where C_1, C_2 are the concentrations in the anode and cathode. This is the measure of the e. m. f. of the cell, the mercury playing the part of an indifferent solvent, and contributing nothing to the effect.

The following numbers, from the experiments of G. Meyer, will serve to illustrate the point (the cell consisted of Zn amalgam (conc.) : $ZnSO_4$: Zn amalgam (dilute)):—

$$C_1 = 0{\cdot}002280, \quad C_2 = 0{\cdot}0000608,$$

and the results obtained were—

	E (*calc.*).	E (*obs.*).
at 12·4°	0·0445	0·0474
60·0°	0·0519	0·0520

Cadmium and copper cells gave similar results. Two points may be noticed with regard to this experiment: first, it brings out clearly the principle, applicable to all concentration cells, that *the electromotive force is proportional to the absolute temperature* (provided the solutions be dilute enough to allow of applying the gaseous laws); second, it proves that the metals in mercury solution are monatomic. For if they were, say, diatomic, the quantity of metal accompanying one coulomb would be the same as before, but it would only produce half as much osmotic pressure in the amalgam; and, hence, only half as much work would be required to restore it to the anode: the e. m. f. would therefore be half that calculated above. The monatomicity of metals in amalgam is confirmed by the results of measurements of the vapour pressure of amalgams.

Next, the concentration of the electrode material may vary if it be a gas absorbed in a solid, particularly hydrogen in platinum or palladium. The e. m. f. of hydrogen with respect to normal solutions of hydrogen salts (acids) quoted above from Neumann's experiments refers to hydrogen at atmospheric pressure dissolved in platinum. Neumann showed experimentally that the e. m. f. between H and acid depends on the concentration of the ionic H in solution, obtaining the following numbers:—

	E.	$E + \frac{RT}{\epsilon} \log \gamma$.
H_{Pt} : $\frac{1}{1}$ HCl	−0·249	−0·255
: $\frac{1}{1}$ H_2SO_4	−0·239	−0·254
: $\frac{1}{1}$ H_3PO_4	−0·205	−0·275
: $\frac{1}{1}$ CH_3COOH	−0·149	−0·289

The degree of dissociation of the four acids, calculated from their conductivities, is about $\gamma = 0{\cdot}80$, 0·54, 0·06, and 0·0038 respectively. If, following the theory of concentration cells, we calculate the e. m. f. between H_{Pt} and a solution containing one gram-atom of H ions per litre, by adding $0{\cdot}05785 \log \gamma$ to the observed values we get the numbers given in the last column of the above table, which are roughly constant.

On the other hand, it is to be expected that, if the electrodes be placed in contact with hydrogen at a pressure greater or less than the atmospheric, the e. m. f. should differ. Hydrogen would saturate the platinum, and an equilibrium would be set up between the gaseous H_2 and the ionic $H^{\cdot}$ in the liquid, in accordance with the law of partition and the law of mass action. Experiments in support of this view appear to be still wanting.

§ 6. Polarization.

When a current is passed through an electrolyte between 'unalterable' electrodes, i. e. plates of platinum, gold, carbon, or other material which conducts but does not dissolve in the solution, the products of electrolysis deposited on the electrodes produce a back electromotive force which shows itself in two ways: (1) it diminishes the total electromotive force in the circuit, and so diminishes the current flowing; (2) if the electrolytic cell be rapidly switched over from the electrolyzing circuit to another not containing a battery, it will cause a current to flow through the latter circuit for a short time until the small amount of active material on the electrodes is used up. That this 'polarization' and its resultant electromotive force is due to the actual presence of matter deposited on the electrodes is shown by the behaviour of plates of platinum black which have absorbed gases, and still better by the experiments of Oberbeck[1] on polarization by solid metals. He showed that when a platinum plate is coated electrolytically with a metal, the electromotive force between it and a solution of that metal only gradually assumes the value observed for the massive metal as the thickness of the deposit grows. The thickness which shows the same properties as the massive substance varies somewhat from one metal to another, but averages about one millionth of a millimetre, i.e. the layer must be a few molecules thick, according to the usual estimates of molecular dimensions[2]. The observed e. m. f. increases as the thickness of the metallic film increases (or as the concentration of the metal increases, it is sometimes said) until that limit is reached.

Consequently, if an increasing electromotive force is applied to an electrolytic cell, at first the only effect is to produce an amount of polarization that balances the applied e. m. f.: there is therefore a momentary current each time the e. m. f. applied by the battery is increased, which stops except for a very small continuous flow due to diffusion of dissolved gases. If the e. m. f. applied is made greater than the maximum polarization of the cell, current then flows continuously, and either gas is evolved or metal deposited as the case may be.

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[1] *Wied.* 31. 336 (1887).

[2] See Thomson and Tait, *Natural Philosophy*, vol. 2, p. 495 (2nd edit.).

The phenomena of polarization are greatly complicated by secondary effects, so that, despite numerous experiments made, the progress towards understanding the subject was not great, especially until the valuable researches of Le Blanc[1].

He measured the total electromotive force required to reach the point of decomposition for numerous electrolytes, and also the separate electromotive forces at the two electrodes, and showed that the maximum polarization at an electrode on which metal is deposited agrees with the e. m. f. observed on immersing a plate of that metal in the liquid, i. e. with the proper reversible e. m. f. of the metal; but when gas is the product of electrolysis, the phenomena are somewhat more complicated because not necessarily reversible.

When platinized platinum electrodes are used in a solution of acid or base the decomposition of water can take place reversibly, because the electrodes have a considerable capacity of absorption for oxygen and hydrogen. If the electrodes where they emerge from the liquid are surrounded by tubes containing oxygen and hydrogen at atmospheric pressure, the arrangement constitutes a reversible cell; when it produces a current, hydrogen ions travel through the liquid towards the cathode, and unite with the oxygen in solution in the platinum to form water. Similarly at the anode water is formed by combination of the hydroxyl ions with dissolved hydrogen; and, at the same time, the electrodes keep saturated by absorbing more gas from their surrounding atmospheres. When current is run through the cell the reverse way, the products of electrolysis are absorbed by the electrodes and excess of gas given off by the platinum. This cell has been studied by Smale[1] and found to possess an e. m. f. of 1·07 volts at 17° and a temperature coefficient 0·00141; these numbers constitute a further proof of reversibility, as they satisfy Helmholtz's equation (cf. next §) for reversible cells, using the known value of the heat of formation of water.

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[1] *Ostw.* 8. 299–330 (1891); 12. 333–358 (1893).

But when plain platinum or gold electrodes are used, they dissolve so little of the gases (immeasurably small quantities) that on electrolysis, oxygen and hydrogen are given off in bubbles at the surface of the liquid, irreversibly, and therefore at the cost of a higher electromotive force. Le Blanc found 1·70 volts as the point of decomposition for all acids and bases that yield oxygen and hydrogen as products. The e. m. f. is independent both of the nature of the electrolyte and its concentration, because it depends essentially on the concentration of the $H^{\cdot}$ and OH' ions in solution, the e. m. f. at the cathode on the hydrogen, that at the anode on the hydroxyl. When the concentration of $H^{\cdot}$ ions is increased, say m-fold (addition of acid), the cathode potential difference is decreased in accordance with the theory of concentration cells, the decrease amounting to $\frac{RT}{\epsilon} \log m$; but the concentration of the OH' ions is necessarily decreased in the same ratio m, since by the law of mass action the product $C_{H^{\cdot}} \times C_{OH'}$ is invariable; this change, however, involves an increase in the potential difference at the anode, the amount of which is also given by the formula $\frac{RT}{\epsilon} \log m$. Hence the *two changes are always in opposite senses, and exactly neutralize*, leaving the total e. m. f. of polarization invariable.

If, however, the acid radicle gives up its charge to the electrode more readily than hydroxyl, the e. m. f. required for decomposition is less than 1·70 volts, and depends on the concentration of the acid. This was shown by Le Blanc to be the case for hydrochloric acid ; thus :—

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[1] *Ostw.* 14. 577-621 (1894).

$\frac{2}{1}$	normal	hydrochloric	acid	1·26 volts.
$\frac{1}{2}$	,,	,,	,,	1·34
$\frac{1}{6}$	,,	,,	,,	1·41
$\frac{1}{16}$	,,	,,	,,	1·62
$\frac{1}{32}$	,,	,,	,,	1·69

Such acid gives off chlorine at the anode ; on further dilution the polarization remains constant at about 1·70 and oxygen is given off instead.

§ 7. Application of Thermodynamics.

Gibbs[1], Helmholtz[2], and others have applied the methods of thermodynamic reasoning with success to the phenomena of galvanic cells, so far as they are reversible. The usual equations of thermodynamics require modification only in the fact that the external work done by the working substance is now electrical, whereas formerly we considered only work done against a fluid pressure.

If from a battery, a quantity H of electricity flows under an electromotive force E, then the electrical work done by the battery is, by definition of electromotive force, $=EH$.

We may accordingly (dealing with an infinitesimal change) write the first law of thermodynamics as

$$dQ = dU + EdH$$

for a system in which the only external work done is the production of an electric current. If this be combined with the equation to the second law

$$dQ = TdS,$$

we get

$$dU = TdS - EdH.$$

This, in a manner precisely similar to that adopted on

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[1] *Trans. Connecticut Acad.* 3. 501.

[2] *Berl. Ber.* 1882, p. 22-39, 825-836.

p. 147, may be transformed into the equation for the free energy

$$dF = -SdT - EdH,$$

from which we deduce

$$\frac{\partial_T S}{\partial H} = \frac{\partial_F E}{\partial T},$$

a *thermodynamic relation* which is the precise analogue of that on p. 146, of which so much use has been made.

Let us now consider the results of this relation with the aid of a particular case, viz. the Daniell cell, as studied by Jahn[1]:

$$\text{Cu} : \text{CuSO}_4 + 100\ \text{H}_2\text{O} : \text{ZnSO}_4 + 100\ \text{H}_2\text{O} : \text{Zn}.$$

The 'heat of reaction' accompanying the substitution of zinc for copper in a solution of the sulphate, measured calorimetrically, is

$$q = 50{,}110 \text{ cals.} = 209{,}910 \text{ joules.}$$

This then is the *loss* of internal energy $(-dU)$ by the cell when one gram-atom of zinc dissolves; and zinc being divalent, this is accompanied by a flow of $2 \times 96{,}540$ coulombs. Hence, *if the electrical energy produced were equal to the chemical energy used up*, the e. m. f. would be given by

$$E \times 193{,}080 = 209{,}910,$$

whence $E = 1{\cdot}0872$ volts. This was the reasoning adopted by Lord Kelvin originally, and it is approximately confirmed for the Daniell cell by experiment, since the e. m. f. is 1·0962 volts at 0°C. It is not exact, however, even in that case, and in others is greatly erroneous, the assumption made above being quite unjustified. If the electrical energy given out by the cell (EdH) were equal to the chemical energy used up $(-dU)$ heat would neither be produced nor consumed in the cell (i. e. $dQ = 0$ in equation). Actually, however, there is a production or consumption of heat in the cell; thus the observed e. m. f. of the Daniell gives as the amount of electrical work done $1{\cdot}0962 \times 2 \times 96{,}540 = 211{,}660$ joules. Of this only 209,910 are supplied by the chemical energy of the materials, so that 1,750 joules are supplied at the expense of the heat energy of the cell, which accordingly falls slightly in temperature by its own activity (apart from any irreversible heating due to internal resistance, which does not enter into the problem).

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[1] *Wied.* 28. 21, 491 (1886).

In order to maintain the temperature of the cell constant therefore, it must be supplied with 1,750 joules of heat for every 193,080 coulombs flowing, and its entropy accordingly increases by $1{,}750 \div T$ (in electrical units). Hence the left-hand side of the thermodynamic relation is

$$\frac{\partial S}{\partial H} = \frac{1750 \div 273}{193080} = 0{\cdot}000033.$$

This then should be equal to the temperature coefficient $\frac{\partial E}{\partial T}$ of the cell, and in fact Jahn found by experiment that the temperature coefficient is 0·000034 volts per 1°, so that even the small difference between the amounts of chemical and electrical energy is satisfactorily accounted for by the theory.

Summarizing the above in algebraic form, we have for the heat supplied to the cell, the difference between the electrical work done when $r\epsilon$ coulombs flow, i.e. $Er\epsilon$, and the heat of reaction q ($r =$ valency, $\epsilon =$ number of coulombs per mol.). Hence

$$\frac{\partial E}{\partial T} = \frac{\partial S}{\partial H} = \frac{Er\epsilon - q}{Tr\epsilon},$$

or

$$q = r\epsilon\left(E - T\frac{\partial E}{\partial T}\right).$$

Mostly the temperature coefficient is negative, so that the chemical energy is incompletely spent in producing electrical work; the cell is heated in action. Another example from Jahn's researches will illustrate this, viz.:—

$$Ag : AgCl : ZnCl_2 + 100\, H_2O : Zn.$$

Here $E = 1{\cdot}0306$, $\dfrac{\partial E}{\partial T} = -0{\cdot}000409$; whence the electrical work $r\epsilon E = 199{,}890$ joules, the calculated value of $q = 220{,}500$ joules, that observed calorimetrically 218,540.

At first sight it might appear in contradiction to the second law of thermodynamics to assume that a galvanic cell can perform work at the expense of its own heat, although at the same temperature as the surroundings. It must be remembered, however, that the law merely denies the possibility of carrying out a *cyclic process* in which even temperature heat is converted into work. A configuration of matter may be such that it is capable of doing a *finite amount* of work at the expense of surrounding heat, while changing its state (e. g. while zinc dissolves); but to restore the original conditions, if the temperature be maintained constant, the same amount of work has to be done on the system; if there were an outstanding amount of work done in the cyclic process, that process might be repeated any number of times, and a finite system would then be the means of converting an *indefinite* amount of even temperature heat into work: that is impossible.

The extreme case in which the electromotive force is not merely the means of converting some heat as well as chemical energy into work, but is exclusively a mechanism for converting heat into work, occurs in all concentration cells. Concentration cells possess no available chemical energy; the osmotic work that might be done in equalizing the concentrations of two solutions would be done at the expense of the sensible heat of the solutions, and what takes place is simply a substitution of electrical for osmotic work, as explained on p. 288. (As with gases: so far as a gas is perfect, it possesses no volume energy, and when it expands merely uses up its own heat in doing external work: see p. 129.) Hence in the thermodynamic equation q (heat of reaction) $= 0$ and

$$0 = r\epsilon\left(E - T\frac{\partial E}{\partial T}\right),$$

or

$$\frac{\partial E}{\partial T} = \frac{E}{T}.$$

Accordingly the e.m.f. of a concentration cell changes by $\frac{1}{273}$ of its value at the freezing point per 1°, or. in other words, is proportional to the absolute temperature.

The same equation may also be applied to the case of the e.m.f. at one junction alone, and gives the thermal value of the reaction that takes place there, viz. ionization. This is important, because it is not possible to determine such thermal values by a calorimetric method, the formation of ions from metal being always associated with some other change (e.g. the return of some other ion to the metallic form). Thus Bouty has measured the e.m.f. of the combination $\mathrm{Cu} : \mathrm{Cu\,SO_4\,.\,Aq}$, and its variation with temperature. The electromotive force at 17° is 0·600, and the value of $\frac{\partial E}{\partial T} = +0{\cdot}00076$. Hence Ostwald[1] calculates the heat of reaction as

$$(0{\cdot}600 - 290 \times 0{\cdot}00076) \times \frac{193080}{4{\cdot}2} = 17{,}500 \text{ cals.}$$

Since the metal is positive to the solution the heat of ionization is negative, i.e. there is an absorption of 17,500 cals. when metallic copper is converted into (divalent-cupric) ions. This result may be written

$$\mathrm{Cu} = \mathrm{Cu}^{\cdot\cdot} - 17{,}500.$$

By combining one such result with ordinary thermal or electromotive measurements, the heats of ionization of all the metals and negative radicles may, step by step, be obtained. Thus the thermal value of the reaction occurring in the Daniell cell is, we have seen, about 50,100. The reaction, however, is merely the replacement of cupric ions by zinc ions, or

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[1] *Ostw.* 11. 501 (1893).

$$Cu^{\cdot\cdot} + Zn = Cu + Zn^{\cdot\cdot} + 50,100.$$

From the last two equations, then, by subtraction we obtain

$$Zn = Zn^{\cdot\cdot} + 32,600.$$

This large positive number is an indication of the strong tendency of zinc to form ions, a tendency which places it high up in the electric 'tension series.'

Again, when zinc dissolves in dilute acid, the reaction is

$$Zn + 2H^{\cdot} = H_2\,(\text{gas}) + Zn^{\cdot\cdot} + 34,200,$$

the heat evolved being 34,200 calories; by combining this with the preceding equation we find

$$H_2\,(\text{gas}) = 2H^{\cdot} - 1,600.$$

Further, when hydrogen and chlorine combine and dissolve in much water to form almost completely dissociated hydrochloric acid, the reaction is accompanied by a large evolution of heat,

$$H_2 + Cl_2 = 2H^{\cdot} + Cl' + 78,600.$$

Hence the formation of chlorine ions takes place according to the equation

$$Cl_2 = 2Cl' + 80,200,$$

so that chlorine has an even stronger tendency to ionize than zinc, being in fact comparable with the alkaline metals.

Oxygen, too, has a strong tendency to form hydroxyl ions, as may be seen from the following equations:—

(1) formation of water from its elements,

$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68,400\ ;$$

(2) neutralization of a strong acid and base,

$$2H^{\cdot} + 2OH' = 2H_2O + 27,000\ ;$$

thence by subtraction

$$H_2 + \tfrac{1}{2}O_2 + H_2O = 2\,H^{\cdot} + 2\,OH' + 41{,}400\,;$$

but since $H_2 = 2\,H^{\cdot} - 1{,}600$, it follows that

$$\tfrac{1}{2}O_2 + H_2O = 2\,OH' + 43{,}000.$$

This may be looked upon as an indication of the oxidizing power of gaseous oxygen; but it must be borne in mind that chemical reactions do not take place strictly according to the amounts of heat evolved in them; those amounts are only a rough guide, and no true measure of affinity.

§ 8. Electromotive Force and Affinity.

Rather it is the electromotive force that is a measure of the affinity brought into play in the reaction that gives rise to it. For the electromotive force is a measure of the work that a reaction is capable of performing, i. e. of the change in the free or available energy of the reacting system. This fact is most clearly illustrated by the behaviour of systems possessing a *transition point.* Consider e. g. the reaction

$$Zn\,SO_4 \cdot 7\,H_2O \rightleftarrows Zn\,SO_4 \cdot 6\,H_2O + H_2O,$$

both hex- and hepta-hydrate are obtainable, but only one of them is stable, viz. at ordinary temperatures the heptahydrate, at higher temperatures the hexhydrate. The transition point is about 39°, i. e. the point at which the two hydrates can exist in equilibrium.

The transition takes place with a certain absorption of heat, which scarcely varies in amount above or below the transition temperature; but the 'affinity' or moving force producing the reaction is at the transition point zero, since there is then no tendency for the reaction to go in either sense, and has opposite signs above and below the transition point. This is shown by the e.m.f. produced; a Clark cell has the construction

$$\mathrm{Zn} : \mathrm{ZnSO_4}\ (\text{sat. sol.}) : \mathrm{Hg_2SO_4} : \mathrm{Hg},$$

and may be made up either with $ZnSO_4 . 7 H_2O$ crystals (the ordinary way), or with $ZnSO_4 . 6 H_2O$. At temperatures below 39° the heptahydrate cell has the higher electromotive force, above that temperature the hexhydrate[1], the two becoming equal at the transition temperature; so that, as remarked in chap. v, such a cell may be used for determining the transition point. If the two cells be joined in opposition to one another, then if the temperature is below 39° current will flow from the heptahydrate to the hexhydrate portion—zinc will be dissolved in the former and deposited in the latter; the quantity of heptahydrate will therefore increase at the expense of the hexhydrate and water of solution. If the temperature be above 39° the same process will occur, but in the opposite sense, so that in either case the stable phase will gain in quantity, and the tendency of the substance to go into the stable form is measured by the e.m.f. of the combined cell, i.e. the 'velocity' of the reaction is proportional to the e.m.f. (the resistance of the cell being regarded as constant), and therefore to the divergence of the temperature from 39°. Thermodynamically considered, in such a cell at the transition point $E = 0$, and therefore

$$q = - r \epsilon T \frac{\partial E}{\partial T}.$$

The sign in this equation indicates—as might be foreseen from general reasoning—that below the transition point the action of the cell is such as to produce the system formed with evolution of heat, above the transition point that formed with absorption of heat.

For further information on transition cells we may refer to van 't Hoff-Cohen, *Studies in Chemical Dynamics* (English edition, 1896, pp. 251–273).

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[1] E. Cohen, *Ostw.* 25. 300 (1898).

The electrometrical method may also be applied to study equilibrium in homogeneous systems. A case of the kind has been very completely worked out by C. Knüpffer[1], viz. the reaction

$$\text{Tl Cl (solid)} + \text{KSCN Aq} \rightleftarrows \text{Tl SCN (solid)} + \text{KCl Aq};$$

this belongs to the somewhat small class of cases in which both reaction constant and electromotive force are of magnitudes accessible to measurement.

Chemical measurements showed that the reaction constant for the system

$$\begin{aligned} K = \frac{C_{\text{KCl}}}{C_{\text{KSCN}}} &= 0{\cdot}85 \text{ at } 39^\circ{\cdot}9, \\ &= 1{\cdot}24 \text{ at } 20^\circ{\cdot}0, \\ &= 1{\cdot}74 \text{ at } 0^\circ{\cdot}8. \end{aligned}$$

The thallium salts, being present as solids, do not enter into the value of K. If then a cell be constructed of the form

Tl amalgam : Tl Cl : KCl : KSCN : Tl SCN : Tl amalgam,

and the ratio between the concentrations in the two electrode vessels be K, the system will be in equilibrium and the e. m. f. zero. If, however, KCl (i. e. chlorine ions) be in excess, there will be an electromotive force such that the right-hand side is the cathode, and current will flow from left to right, until the amount of KSCN is so far increased and that of K Cl reduced that equilibrium is restored. If at any time the ratio of concentration

$$\frac{C_{\text{K Cl}}}{C_{\text{KSCN}}} = a,$$

the electromotive force, as was shown by van 't Hoff, is

$$E = \frac{RT}{\epsilon} \log \frac{K}{a} \cdot$$

---

[1] *Ostw.* 26. 255 (1898).

This may perhaps most easily be seen by applying the reasoning already used for concentration cells to reduce the cell in question to the equilibrium state of no e. m. f.

Knüpffer measured the e. m. f. of such cells with values of a varying from 0·8 to 1·6, and found it agree to within a millivolt with the numbers calculated from van 't Hoff's formula.

INDEX

Absorption coefficient, 237.
— spectrum, 121.
Acetamide, decomposition of, 189.
Acetylene, combustion of, 187.
Acids, heat of dissociation of, 274.
— strength of, 168, 188.
Additive properties, 92.
Affinity, 276.
— and electromotive force, 302.
Alkaloids, strength of, 170.
AMAGAT, 81, 86.
Amalgams, electromotive force of, 290.
Ammonia compounds of salts, 215.
Ammonium carbamate, dissociation of, 51, 234.
— nitrate crystals, 225.
— sulphydrate, dissociation of, 233.
Ampere, 56.
ANDREAE, 221.
Anion, influence of, 286.
ARRHENIUS, 53, 165, 171.
— and WALKER, 174.
Arsine, dissociation of, 179.
Association, factor of, 115.
Asymmetric carbon atom, 119.
Atmosphere, 5.
Atomic heat, 10.
— refraction, 100.
— viscosity, 110.
— volume, 91.
Atomicity of metals, 291.
AULICH, 239.
Avidity, 167, 188.
AVOGADRO, 7, 12.

Barium sulphate, solubility of, 271.
BECKMANN, 35, 43.
Benzene, vapour pressure of, 39.
Benzoic acid, molecular weight in solution, 240.
BERTHELOT, 250, 252.
— and OGIER, 273.
— and PÉAN DE ST. GILLES, 163.
— and VIEILLE, 199.
BERTHELOT, D., 7.
Bimolecular reaction, 183.
BODENSTEIN, 159, 196.
Boiling point, determination of, 37.
— of solutions, 32.
— of water and pressure, 204.
BOLTZMANN, 103.
BOUTY, 300.
BOYS, 256.
α-bromisocinnamic acid, solubility of, 236.
BRÜHL, 99.
BUNSEN, 237, 256.
Bunsen calorimeter, 255.

CAILLETET and COLARDEAU, 82.
— and MATHIAS, 89.
Calcium carbonate, dissociation of, 222.
Calorie, 9.
Calorimetric bomb, 252.
Calorimetry, 249.
Capacity, electrical, 102.
Capillary electrometer, 280.
Carbon monoxide and steam, action of, 201.
Catalytic action, 165.
CAUCHY, 102.
C.G.S. system, 2.
Characteristic equation, 8, 76.
Chloral hydrate, dissociation of, 52.
Clark cell, 279, 303.
CLAUSIUS, 104, 126.
Coefficient of absorption, 122.
COHEN, E., 303.
Combustion, temperature of, 199.
Concentration, 26.
— cells, 278, 287, 300.
Condensed system, 210.
Conductivity, 60.
— measurement of, 62.
— molecular, 66.
— partial, 70, 72.
CONRADY, 99.
Constitutive properties, 116.
Convergence temperature, 45.
COOKE, J. P., 15.
Copper-calcium acetate, transition of, 266.
— sulphate, vapour pressure of, 268.
Correction for air displacement, 78.
Corresponding states, 86.
Coulomb, 56.
Criterion of equilibrium, 139.
Critical point, 81.
— of mixture, 226.
Cryohydric point, 220.
Cupric chloride, heat of solution of, 266.
Cyamelide, polymerization of, 186.

Daniell cell, 297.
DAY, 9.
Decinormal gas, 184.
Density, at critical point, 90.
— measurement of, 77.
— of water, 79.
DEVILLE, 235.
Dibromosuccinic acid, decomposition of, 195.
Dichloracetic acid, avidity of, 169.
— dissociation of, 55.
Dielectric constant, 102, 203.
— measurement of, 105.
DIETERICI, 256.
Dilatometer, 79, 224.
Dilution, 28.
— heat of, 258.
Discontinuity of curves, 218.
Dispersion, atomic, 100.
— formula, 102.
Dissociation constant, 50, 69.
— — of water, 171, 174.
— degree of, 49.
— electrolytic, 52, 164
— of gases, 47.
— pressure, 222, 233.

Dropping electrodes, 281.
Dulong and Petit, 10.
Dumas, 17.
Dye-stuffs, theory of, 123.
Dynamical equivalent of heat, 127.

Elasticity, 5, 8.
Electro-chemical equivalent, 56.
Electrolysis, laws of, 56.
Electrolytes with a common ion, 166.
Electrolytic dissociation, 52, 164.
Electromotive force, 58.
— forces, single, 283, 287.
Endo- and exo-thermic reactions, 247.
Energy, 3.
Entropy, 134, 198.
Esterification, 162, 177, 192, 273.
Esters, decomposition of, 189.
Ewan, T., 202.
Excess influence on equilibrium, 163, 233.
Expansion, coefficient of, 80.
Explosion, 196.

Factor, van 't Hoff's, 54.
False equilibrium, 200.
Faraday, 56.
Fluid pressure, 128.
Free energy, 147, 297.
Freedom, degrees of, 206.
Freezing point, depression of, 41.
— determination of, 43, 44.
Frowein, 268.

Galvanic cell, 277.
Gas battery, 294.
— characteristic equation of a, 76, 84.
— constant, 7.
— density, 13.
— energy of a, 130.
Gases, conduction in, 59.
— dielectric constant of, 103.
— dissociation of, 47.
— laws of, 6.
— specific heat of, 131, 248.
Gay-Lussac, 20.
Gibbs, 206, 296.
Gladstone and Dale, 98.
Glauber salt, 216.
Gravity, 4.
Guillaume, 254.
Guldberg and Waage, 142.

Hamburger, 28.
Heat of combustion, 247.
— evaporation of solutions, 267.
— reaction, 10, 244.
— — and temperature, 248.
Helmholtz, 281, 287, 296.
Hemihedry, 120.
Henry, 237.
Hittorf, 71.
Hoff, van 't, 23, 53, 119, 151, 165, 179, 186, 191, 196, 266, 269, 305.
Hofmann, 20.
Hoitsema, 201, 248.
Homogeneous system, 153.
Horstmann, 234.
Hydrates, 215, 221.
Hydriodic acid, decomposition of, 158, 177, 193, 196.
Hydrogen electrode, 292.
Hydrolysis, 172.
Hyoscyamine, inversion of, 190.

Independent variation, 206.
Inflammation, temperature of, 197.
Internal energy, 127.
— latent heat, 245.
Inversion of sugar, 165.
Ionic conductivities, 72.
— velocities, 74.
Ionization, heat of, 300.
Iron, reduction of, 234.
Isentropic, 132.
Isothermal, 86, 131.

Jahn, 297.
Jellet, 169.
Joubert, 202.
Joule, 130.

Kelvin, 281, 297.
Knoblauch, 192.
Knüpffer, C., 304.
Kohlrausch, 65, 70, 72, 171.
Kooij, 179.
Kopp, 91.

Landolt, 98.
Law of correspondence, 86, 88.
— mass action, 142, 153, 232.
— partition, 239.
Laws of thermodynamics, 126.
Le Blanc, 294.
Le Chatelier, 222.
Leduc, 15.
Lehfeldt, 229.
Lehmann, 225.
Limiting conductivity, 70.
— volume, 85.
Lippmann, 280.
Loewel, 216.
Lorentz, H., 98, 104.
Lorenz, L., 98, 104.

Magnetic rotation, 118.
Mallard and Le Chatelier, 199.
Maxwell, 103, 126, 146.
Melting point of ice, 264.
— mixtures, 220.
— vapour pressure at, 39.
Menschutkin, 203.
Method of mixture, 249.
Meyer, G., 291.
Meyer, V., 18.
Mho, 60.
Mixtures, refractive index of, 101.
Moissan and Gautier, 16.
Mol, 8.
Molecular depression of the freezing point, 43.
— dimensions, 293.
— elevation of the boiling point, 35, 38.
— kinetic energy, 24.
— surface energy, 113.
— viscosity, 109.
— weight of liquids, 115.
Monochloracetic acid, dissociation of, 68.
Monomolecular reaction, 179.
Morley, E. W., 15.
Mutual solubility, 227.

Natanson, E. and L., 48.
Nernst, W., 45, 105, 239, 253, 290.
Neumann, B., 286.
Neutralisation, 170, 273.
Nilson and Petterson, 19.
Nitrogen tetroxide, dissociation of, 49, 158, 176, 272.
Normal electrode, 282.
Noyes, 236.
— and Cottle, 185.

Oberbeck, 293.
Ohm's law, 60.
Osmotic pressure, 23.
— and temperature, 270.
Ostwald, W., 68, 73, 107, 168, 171, 189, 205, 250, 282, 300.
— and Nernst, 59.
Oxygen, density of, 7.
— and hydrogen, combination of, 196, 197, 199, 200.

PARKAU, 221.
PASCHEN, F., 284.
PERKIN, W. H., 118.
PFEFFER, 25.
Phase, 204.
Phenol-water mixtures, 229.
Phosphine, oxidation of, 187.
Phosphorus, oxidation of, 202.
PICKERING, 253, 262.
Plasmolysis, 28.
Polarization, electric, 284, 292.
— of light, 116.
Potassium chloride, conductivity of, 65.
— dissociation of, 67.
Potentiometer, 278.
Pressure, 5.
— on condensed systems, 211.
Progressive combustion, 198.
PULFRICH, 96.
Pyknometer, 77.

Quadruple point, 219, 230.

Racemic acid, 120
Radiation correction, 255.
RAMSAY and SHIELDS, 111.
— and YOUNG, 22.
RAOULT, 31, 269.
RAYLEIGH, 15.
Reaction constant, 143.
— — and electromotive force, 304.
— — and velocity of reaction, 192.
— — influence of temperature on, 149, 263.
— — maximum of, 201.
— — reduced, 242.
— degree of, 149.
Rectilinear diameter, law of, 89.
Reduced concentration, 242.
— volume, pressure, temperature, 85.
Reduction of silver, 185.
Refraction, atomic, 100.
Refractive index, 93.
Refractivity, 98.
Refractometer, 96.
REGNAULT, 13.
REICHER, 211.
Reversibility, thermodynamic, 133, 285.
Reversible reaction, 154.
RICHARDS, 219.
RIECKE, 176.
Rigidity, 6.
ROOZEBOOM, 229.
Rotation of polarized light, 118.
ROWLAND, 9.
RUDOLPHI, 165.

Saponification, 183, 190.
Saturation pressure, 81, 194.
SCHÜTZE, 123.
Semi-permeable membrane, 25.
SHIELDS, 173.
Siemens' unit, 65.
Silver chloride, solubility of, 271.
— nitrate, solubility of, 228.
Simple solubility, 227.
SIMS, 238.
SMALE, 295.
Sodium monochloracetate, decomposition of, 191.
— nitrate, heat of solution of, 261.
Solid solution, 204.
Solids, specific heat of, 249.
Solubility and heat of solution, 270.
— and vapour pressure, 218.
Solubility, coefficient of, 237.
— measurement of, 223.
— of salts, 216.
— — with common ion, 236.
— real and apparent, 235.
Solution, heat of, 258.
Solutions, boiling point of, 32.
— theory of, 23.
— vapour pressure of, 29.
Spectrometer, 94.
SPRING, 206.
Stability, reversal of, 40, 209
STOHMANN, 250.
Sugar, inversion of, 165, 180.
— osmotic pressure of, 27.
Sulphur dioxide and water, 229.
— dissociation of, 176.
— equilibrium of, 211.
Sulphuric acid and water, heat of mixture, 262.
Surface tension, 8, 111.

Temperature coefficient of electromotive force, 291, 298.
— coefficient of refractive index, 96.
Temperatures, constant, 22.
Tensimeter, 223.
Therm, 9.
Thermal capacity and heat of reaction, 248.
— capacity of solutions, 254.
Thermodynamic model, 214.
— potential, 147.
— relation, 146, 297.
Thermostat, 64.
THOMSEN, J., 250, 262, 274.
THORPE and RODGER, 108.
Transference ratio, 71, 289.
Transition cell, 303.
— heat of, 257, 264.
— point, 209, 217, 231.
— — and pressure, 264.
— — measurement of, 222.
TRAUBE, J., 93.
Trimolecular reaction, 184.

Units, 2.

Vapour density, 17.
— pressure at melting point, 39.
— — of mixtures, 226.
— — of salt hydrates, 217, 221.
— — of solutions, 29, 267.
Velocity of explosive wave, 198.
— of reaction, 155, 178, 180.
— — and reaction constant, 192.
— — effect of concentration on, 186.
— — temperature coefficient of, 194.
Viscosity, 6, 106.
Volume energy, 129.
DE VRIES, 28.

WAALS, VAN DER, 8, 83.
Water, dissociation of, 171, 274.
— heat of formation of, 246.
Wave length, 99.
Wheatstone's bridge, 62.
WILDERMANN, 46, 55.
WILL and BREDIG, 190.
WILLIAMSON, 142.
WYS, 171.

YOUNG, S., 82, 87.
— and THOMAS, 20.

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